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(54) Title: FUNGICIDAL COMPOSITIONS

$$X \xrightarrow{E} Y Z$$

$$X \xrightarrow{G} W$$

$$X \xrightarrow{R^2}$$

(57) Abstract

Advantageous fungicidal combinations are disclosed comprising (1) at least one compound selected from the compounds of Formula (I), N-oxides and agriculturally suitable salts thereof, and (2) at least one compound selected from (a) compounds of Formula (II), N-oxides, and agriculturally suitable salts thereof, wherein E¹ is (i) or (ii); and R²⁸ is H or phenoxy; and (b) compounds that control fungal disease by inhibiting the sterol biosynthesis pathway; wherein A, E, W, X, Y, Z and R² are as defined in the disclosure. Included are fungicidal compositions comprising fungicidally effective amounts of the compound combinations of the invention and a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of the compound combinations of the invention.

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TITLE FUNGICIDAL COMPOSITIONS BACKGROUND OF THE INVENTION

Fungicides that effectively control plant diseases are in constant demand by growers. Plant diseases are highly destructive, difficult to control and quickly develop resistance to commercial fungicides. Combinations of pesticides are often used to facilitate disease control, to broaden spectrum of control and to retard resistance development. It is recognized in the art that the advantages of particular pesticide combinations can often vary, depending on such factors as the particular plant and plant disease to be treated, and the treatment conditions.

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International Patent Application WO 95/14009 discloses certain triazolone compounds as fungicides including 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one (Formula Ia, an example of the compounds of Formula I defined herein). International Patent Application WO 90/12791 discloses certain oxazolidinone compounds as fungicides including 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone (Formula IIa, an example of the compounds of Formula II defined herein). European Patent Application EP-A-551048 discloses 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4*H*-imidazol-4-one (Formula IIb, an example of the compounds of Formula II defined herein). European Patent Application EP-A-68813 discloses certain triazole compounds as fungicides (e.g., flusilazole). European Patent Application EP-A-40345 discloses certain triazole compounds as fungicides (e.g., tebuconazole).

Research Disclosure 1996, No. 38829, 487-490 discloses synergistic mixtures of 5-methyl-5-(4-phenoxyphenyl)-3-(phenylamino)-2,4-oxazolidinedione with fungicides, insecticides and herbicides. International Patent Application WO 96/03044 discloses synergistic mixtures of 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4*H*-imidazol-4-one with fungicides.

SUMMARY OF THE INVENTION

This invention is directed to fungicidal combinations (e.g., mixtures) comprising (1) at least one compound selected from the compounds of Formula I (including all geometric and stereoisomers), N-oxides, and agriculturally suitable salts thereof,

wherein

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E is selected from:

i) 1,2-phenylene optionally substituted with R³ or both R³ and R⁴;

ii) naphthalenediyl, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalenediyl optionally substituted with R3 or both R3 and R4; and iii) a ring system selected from 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes one or two Q as ring members and optionally includes one or two ring members independently selected from C(=O) and S(O)₂, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic heterocyclic ring system optionally substituted with R3 or both R3 and R4;

A is O, S, N, NR⁵ or CR¹⁴; 20

> G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A;

W is O, S, NH, $N(C_1-C_6 \text{ alkyl})$ or $NO(C_1-C_6 \text{ alkyl})$;

X is H, OR¹, S(O)_mR¹, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₃-C₆ cycloalkyl, cyano, NH₂, NHR¹, N(C₁-C₆ alkyl)R¹, NH(C₁-C₆ alkoxy) or $N(C_1-C_6 \text{ alkoxy})R^1$;

R¹ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C2-C6 alkynyl, C2-C6 haloalkynyl, C3-C6 cycloalkyl, C2-C4 alkylcarbonyl or C2-C4 alkoxycarbonyl;

R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C2-C6 alkynyl, C2-C6 haloalkynyl, C3-C6 cycloalkyl, C2-C4 alkylcarbonyl, C₂-C₄ alkoxycarbonyl, hydroxy, C₁-C₂ alkoxy or acetyloxy;

	R ³ and R ⁴ are each independently halogen; cyano; nitro; hydroxy; C ₁ -C ₆ alkyl;
	C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl;
	C_2 - C_6 haloalkynyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyloxy;
	C_2 - C_6 alkynyloxy; C_1 - C_6 alkylthio; C_1 - C_6 alkylsulfinyl;
5	C ₁ -C ₆ alkylsulfonyl; formyl; C ₂ -C ₆ alkylcarbonyl; C ₂ -C ₆ alkoxycarbonyl;
_	$NH_2C(O)$; $(C_1-C_4 \text{ alkyl})NHC(O)$; $(C_1-C_4 \text{ alkyl})_2NC(O)$; $Si(R^{25})_3$;
	Ge(R ²⁵) ₃ ; (R ²⁵) ₃ Si-C≡C-; or phenyl, phenylethynyl, benzoyl, or
	phenylsulfonyl each substituted with R ⁸ and optionally substituted with one
	or more R ¹⁰ ; or
10	when E is 1,2-phenylene and R ³ and R ⁴ are attached to adjacent atoms, R ³ and R ⁴
	can be taken together as C ₃ -C ₅ alkylene, C ₃ -C ₅ haloalkylene,
	C ₃ -C ₅ alkenylene or C ₃ -C ₅ haloalkenylene each optionally substituted with
	1-2 C ₁ -C ₃ alkyl;
	R ⁵ is H, C ₁ -C ₆ alkyl, C ₁ -C ₆ haloalkyl, C ₂ -C ₆ alkenyl, C ₂ -C ₆ haloalkenyl,
15	C ₂ -C ₆ alkynyl, C ₂ -C ₆ haloalkynyl, C ₃ -C ₆ cycloalkyl, C ₂ -C ₄ alkylcarbonyl
	or C_2 - C_4 alkoxycarbonyl;
	Y is -O-, $-S(O)_n$ -, $-NR^{15}$ -, $-C(=O)$ -, $-CH(OR^{15})$ -, $-CHR^6$ -, $-CHR^6$ CHR ⁶ -,
	-CR6=CR6-, -C=C-, -CHR15O-, -OCHR15-, -CHR15S(O) _n -, -S(O) _n CHR15-,
	$-CHR^{15}O-N=C(R^7)-$, $-(R^7)C=N-OCH(R^{15})-$, $-C(R^7)=N-O-$, $-O-N=C(R^7)-$,
20	$-CHR^{15}OC(=O)N(R^{15})-$, $-CHR^{15}OC(=S)N(R^{15})-$, $-CHR^{15}OC(=O)O-$,
	-CHR ¹⁵ OC(=S)O-, -CHR ¹⁵ OC(=O)S-, -CHR ¹⁵ OC(=S)S-,
	$-CHR^{15}SC(=O)N(R^{15})-$, $-CHR^{15}SC(=S)N(R^{15})-$, $-CHR^{15}SC(=O)O-$,
	-CHR ¹⁵ SC(=S)O-, -CHR ¹⁵ SC(=O)S-, -CHR ¹⁵ SC(=S)S-,
	-CHR ¹⁵ SC(=NR ¹⁵)S-, -CHR ¹⁵ N(R ¹⁵)C(=O)N(R ¹⁵)-,
25	-CHR ¹⁵ O-N(R ¹⁵)C(=O)N(R ¹⁵)-, -CHR ¹⁵ O-N(R ¹⁵)C(=S)N(R ¹⁵)-,
	-CHR ¹⁵ O-N=C(R ⁷)NR ¹⁵ -, -CHR ¹⁵ O-N=C(R ⁷)OCH ₂ -,
	$-CHR^{15}O-N=C(R^7)-N=N-, -CHR^{15}O-N=C(R^7)-C(=0)-,$
	$-CHR^{15}O-N=C(R^7)-C(=N-A^2-Z^1)-A^1-$
	-CHR ¹⁵ O-N=C(R ⁷)-C(R ⁷)=N-A ² -A ³ -, -CHR ¹⁵ O-N=C(-C(R ⁷)=N-A ² -Z ¹)-,
30	$-CHR^{15}O-N=C(R^7)-CH_2O-$, $-CHR^{15}O-N=C(R^7)-CH_2S-$,
	$-O-CH_2CH_2O-N=C(R^7)-$, $-CHR^{15}O-C(R^{15})=C(R^7)-$, $-CHR^{15}O-C(R^7)=N-$,
	$-CHR^{15}S-C(R^7)=N-, -C(R^7)=N-NR^{15}-, -CH=N-N=C(R^7)-,$
	-CHR ¹⁵ N(R ¹⁵)-N=C(R ⁷)-, -CHR ¹⁵ N(COCH ₃)-N=C(R ⁷)-,
	$-OC(=S)NR^{15}C(=O)-$, $-CHR^6-C(=W^1)-A^1-$, $-CHR^6CHR^6-C(=W^1)-A^1-$,
35	$-CR^{6}=CR^{6}-C(=W^{1})-A^{1}-$, $-C=C-C(=W^{1})-A^{1}-$, $-N=CR^{6}-C(=W^{1})-A^{1}-$ or a
	direct bond; and the directionality of the Y linkage is defined such that the
	moiety depicted on the left side of the linkage is bonded to E and the moiety
	on the right side of the linkage is bonded to Z;

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 Z^1 is H or $-A^3$ -Z: W^1 is O or S: A¹ is O, S, NR¹⁵ or a direct bond; A² is O, NR¹⁵ or a direct bond; 5 A^3 is -C(=O)-, -S(O)₂- or a direct bond; each R⁶ is independently H, 1-2 CH₃, C₂-C₃ alkyl, C₁-C₃ alkoxy, C3-C6 cycloalkyl, formylamino, C2-C4 alkylcarbonylamino, C2-C4 alkoxycarbonylamino, NH2C(O)NH, (C1-C3 alkyl)NHC(O)NH, (C₁-C₃ alkyl)₂NC(O)NH, N(C₁-C₃ alkyl)₂, piperidinyl, morpholinyl, 10 1-2 halogen, cyano or nitro; each R⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylthio, C₁-C₆ haloalkylsulfinyl, C₁-C₆ haloalkylsulfonyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, 15 C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, halogen, cyano, nitro, hydroxy, amino, $NH(C_1-C_6 \text{ alkyl}), N(C_1-C_6 \text{ alkyl})_2 \text{ or morpholinyl};$ each Z is independently selected from: i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl and C₂-C₁₀ alkynyl each substituted with 20 R^9 and optionally substituted with one or more R^{10} ; ii) C₃-C₈ cycloalkyl, C₃-C₈ cycloalkenyl and phenyl each substituted with R^9 and optionally substituted with one or more R^{10} ; iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic and fused tricyclic nonaromatic heterocyclic ring systems and 5 to 25 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each 30 nonaromatic or aromatic heterocyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰; iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing 35 one or two nonaromatic rings that each include one or two Q as ring members and one or two ring members independently selected from C(=O)

> and S(O)2, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R9 and optionally substituted with

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one or more R¹⁰; and

 R^{12} , or both R^{11} and R^{12} ;

- v) adamantyl substituted with R⁹ and optionally substituted with one or more R¹⁰:
- each Q is independently selected from the group -CHR¹³-, -NR¹³-, -O- and -S(O)_n-;
- R⁸ is H, 1-2 halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy,

 C₁-C₆ haloalkoxy, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl,

 C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl,

 C₁-C₆ alkylsulfonyl, C₃-C₆ cycloalkyl, C₃-C₆ alkenyloxy,

 CO₂(C₁-C₆ alkyl), NH(C₁-C₆ alkyl), N(C₁-C₆ alkyl)₂, cyano, nitro,

 SiR¹⁹R²⁰R²¹ or GeR¹⁹R²⁰R²¹:
- R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy;

 C₁-C₆ haloalkoxy; C₂-G₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl;

 C₁-C₆ alkylthio; C₁-C₆ haloalkylthio; C₁-C₆ alkylsulfinyl;

 C₁-C₆ alkylsulfonyl; C₃-C₆ cycloalkyl; C₃-C₆ alkenyloxy;

 CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; -C(R¹⁸)=NOR¹⁷;

 cyano; nitro; SF₅; SiR²²R²³R²⁴; or GeR²²R²³R²⁴; or R⁹ is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl, or pyrimidinyloxy each optionally substituted with one of R¹¹,
 - each R 10 is independently halogen, C $_1$ -C $_4$ alkyl, C $_1$ -C $_4$ haloalkyl, C $_1$ -C $_4$ alkoxy, nitro or cyano; or
 - when R⁹ and an R¹⁰ are attached to adjacent atoms on Z, R⁹ and said adjacently attached R¹⁰ can be taken together as -OCH₂O- or -OCH₂CH₂O-; each CH₂ group of said taken together R⁹ and R¹⁰ optionally substituted with 1-2 halogen; or
 - when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is

 -CHR¹⁵O-N=C(R⁷)-, -O-N=C(R⁷)-, -O-CH₂CH₂O-N=C(R⁷)-,

 -CHR¹⁵O-C(R¹⁵)=C(R⁷)-, -CH=N-N=C(R⁷)-, -CHR¹⁵N(R¹⁵)-N=C(R⁷)- or

 -CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as -(CH₂)_r-J- such that J is attached to Z;
 - J is -CH₂-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -N(R¹⁶)CH₂- or -CH₂N(R¹⁶)-; each CH₂ group of said J optionally substituted with 1 to 2 CH₃;
- R¹¹ and R¹² are each independently 1-2 halogen; C₁-C₄ alkyl; C₁-C₄ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₂-C₆ alkoxyalkyl; C₂-C₆ alkylthioalkyl; C₃-C₆ alkoxyalkynyl; C₇-C₁₀ tetrahydropyranyloxyalkynyl; benzyloxymethyl; C₁-C₄ alkoxy;

C₁-C₄ haloalkoxy; C₃-C₆ alkenyloxy; C₃-C₆ haloalkenyloxy; C₃-C₆ alkynyloxy; C₃-C₆ haloalkynyloxy; C₂-C₆ alkoxyalkoxy; C₅-C₉ trialkylsilylalkoxyalkoxy; C₂-C₆ alkylthioalkoxy; C₁-C₄ alkylthio; C₁-C₄ haloalkylthio; C₁-C₄ alkylsulfinyl; C₁-C₄ haloalkylsulfinyl; C₁-C₄ alkylsulfonyl; C₁-C₄ haloalkylsulfonyl; C₃-C₆ alkenylthio; 5 C₃-C₆ haloalkenylthio; C₂-C₆ alkylthioalkylthio; nitro; cyano; thiocyanato; hydroxy; $N(R^{26})_2$; SF_5 ; $Si(R^{25})_3$; $Ge(R^{25})_3$; $(R^{25})_3Si-C=C-$; $OSi(R^{25})_3$; $OGe(R^{25})_3$; $C(=O)R^{26}$; $C(=S)R^{26}$; $C(=O)OR^{26}$; $C(=S)OR^{26}$; $C(=O)SR^{26}$; $C(=S)SR^{26}$; $C(=O)N(R^{26})_2$; $C(=S)N(R^{26})_2$; $OC(=O)R^{26}$; $OC(=S)R^{26}$; $SC(=O)R^{26}$; $SC(=S)R^{26}$; $N(R^{26})C(=O)R^{26}$; $N(R^{26})C(=S)R^{26}$; 10 $OC(=O)OR^{27}$; $OC(=O)SR^{27}$; $OC(=O)N(R^{26})$; $SC(=O)OR^{27}$; $SC(=O)SR^{27}$; $S(O)_2OR^{26}$; $S(O)_2N(R^{26})_2$; $OS(O)_2R^{27}$; $N(R^{26})S(O)_2R^{27}$; or phenyl, phenoxy, benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or pyridinylethynyl, each optionally substituted with halogen, C₁-C₄ alkyl, 15 C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; each R¹³ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; R¹⁴ is H, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C2-C6 haloalkenyl, C2-C6 alkynyl, C2-C6 haloalkynyl or C3-C6 cycloalkyl; 20 each R¹⁵ is independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; or when Y is -CHR¹⁵N(R¹⁵)C(=0)N(R¹⁵)-, the two R¹⁵ attached to nitrogen atoms on said group can be taken together as -(CH₂)_s-; or 25 when Y is -CHR¹⁵O-N=C(R⁷)NR¹⁵-, R⁷ and the adjacently attached R¹⁵ can be taken together as -CH₂-(CH₂)_S-, -O-(CH₂)_S-, -S-(CH₂)_S- or -N(C₁-C₃ alkyl)-(CH₂)₅-; with the directionality of said linkage defined such that the moiety depicted on the left side of the linkage is bonded to the carbon and the moiety on the right side of the linkage is bonded to the 30 nitrogen: R¹⁶, R¹⁷ and R¹⁸ are each independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano; R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are each independently C_1 - C_6 alkyl, 35 C₂-C₆ alkenyl, C₁-C₄ alkoxy or phenyl; each R^{25} is independently C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl,

C₁-C₄ alkoxy or phenyl;

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each R²⁶ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

each R²⁷ is independently C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

m, n and p are each independently 0, 1 or 2;

r is 0 or 1; and

s is 2 or 3;

and (2) at least one compound selected from (a) compounds of Formula II (including all geometric and stereoisomers), N-oxides, and agriculturally suitable salts thereof,

wherein

E1 is

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the directionally of the E¹ linkage is defined such that the moiety depicted on the left side of the linkage is bonded to carbon and the moiety on the right side is bonded to nitrogen; and

R²⁸ is H or phenoxy;

and (b) compounds that control fungal disease by inhibiting the sterol biosynthesis pathway. This invention provides agricultural compositions containing these combinations and the use of the combinations as fungicides. Advantageous compositions include those where component (1) and component (2) are present in a fungicidally effective amount and the mole ratio of component (1) to component (2) is from about 15:1 to 1:15. Advantageous methods include those where component (1)

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and component (2) are added in amounts sufficient to provide a fungicidal effectiveness greater than the sum of the fungicidal effectivenesses provided by those amounts of said components taken independently.

DETAILS OF THE INVENTION

Combinations of fungicides are used in accordance with this invention to facilitate disease control and to retard resistance development. Suitable compositions and methods are provided.

For example, this invention also provides methods for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected one of the following:

- A) an effective amount of a fungicidal composition comprising component (1), component (2), and at least one of a surfactant, a solid diluent or a liquid diluent;
- B) (i) an effective amount of a first composition comprising component (1), and at least one of a surfactant, solid or liquid diluent; and (ii) an effective amount of a second composition comprising component (2), and at least one of a surfactant, a solid diluent or a liquid diluent; said first and second compositions applied sequentially in any order; or
- C) an effective amount of a physical mixture of the first and second compositions as defined in B above.

The mole ratio of the compound(s) of component (1) to the compound(s) of component (2) applied is normally from about 15:1 to 1:15, and the compound(s) of component (1) and the compound(s) of component (2) are normally applied in amounts effective to provide control of the fungal disease which is greater than the additive control of that fungal disease provided by the compound(s) of component (1) and the compound(s) of component (2) individually.

In the above recitations, the term "alkyl", used in compound words such as "alkylthio" or "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers. The term "alkyl", used alone includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl isomers. The term "1-2 CH₃" indicates that the substituent can be methyl (i.e., Me) or, when there is a hydrogen attached to the same atom, the substituent and said hydrogen can both be methyl. "Alkenyl" includes straight-chain or branched alkenes such as vinyl, 1-propenyl, 2-propenyl and the different butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl and decenyl isomers. "Alkenyl" also includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl,

hexynyl, heptynyl, octynyl, nonynyl and decynyl isomers. "Alkynyl" can also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl.

"Alkylene" denotes a straight-chain alkanediyl. Examples of "alkylene" include CH₂CH₂CH₂, CH₂CH₂CH₂CH₂ and CH₂CH₂CH₂CH₂CH₂. "Haloalkylene" denotes a halogen substituted alkylene. Examples of "haloalkylene" include CH₂CH(CF₃), CH₂CF₂CH₂ and CH₂CH(CCl₃). "Alkenylene" denotes a straight-chain alkenediyl containing one olefinic bond. Examples of "alkenylene" include CH₂CH=CH, CH₂CH=CH, CH₂CH=CHCH₂ and CH₂CH=CHCH₂CH₂. "Haloalkenylene" denotes a halogen substituted alkenylene. Examples of "haloalkenylene" include CH₂CCl=CCl and CH=C(CF₃).

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"Alkoxy" includes, for example, methoxy, ethoxy, n-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkoxyalkyl" denotes alkoxy substitution on alkyl. Examples of "alkoxyalkyl" include CH₃OCH₂, CH₃OCH₂CH₂, CH₃CH₂OCH₂CH₂CH₂OCH₂ and CH₃CH₂OCH₂CH₂. "Alkoxyalkoxy" denotes alkoxy substitution on alkoxy. Examples of "alkoxyalkoxy" include CH₃OCH₂O, (CH₃)₃COCH₂O and CH₃OCH₂CH₂O. "Alkenyloxy" includes straight-chain or branched alkenyloxy moieties. Examples of "alkenyloxy" include H₂C=CHCH₂O, (CH₃)₂C=CHCH₂O, (CH₃)CH=CHCH₂O, (CH₃)CH=C(CH₃)CH₂O and CH₂=CHCH₂CH₂O. "Alkynyloxy" includes straight-chain or branched alkynyloxy moieties. Examples of "alkynyloxy" include HC=CCH₂O, CH₃C=CCH₂O and CH₃C=CCH₂O. "Alkoxyalkynyl" includes straight-chain or branched alkoxyalkynyl. "Alkoxyalkynyl" includes straight-chain or branched alkoxyalkynyl moieties. Examples of "alkoxyalkynyl" include (CH₃)₂CHOCH₂C=C and CH₃OCH₂C=C.

"Alkylthio" includes branched or straight-chain alkylthio moieties such as 25 methylthio, ethylthio and the different propylthio, butylthio, pentylthio and hexylthio isomers. "Alkylthioalkyl" denotes alkylthio substitution on alkyl. Examples of "alkylthioalkyl" include CH₃SCH₂, CH₃SCH₂CH₂, CH₃CH₂SCH₂, CH₃CH₂CH₂CH₂SCH₂ and CH₃CH₂SCH₂CH₂. "Alkylthioalkoxy" denotes alkylthio substitution on alkoxy. Examples of "alkylthioalkoxy" include CH₃SCH₂O and CH₃CH₂SCH₂CH₂O. "Alkylthioalkylthio" denotes alkylthio substitution on alkylthio. 30 Examples of "alkylthioalkylthio" include CH₃SCH₂S and CH₃SCH₂CH₂S. "Alkylsulfinyl" includes both enantiomers of an alkylsulfinyl group. Examples of "alkylsulfinyl" include CH₃S(O), CH₃CH₂S(O), CH₃CH₂CH₂S(O), (CH₃)₂CHS(O) and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of "alkylsulfonyl" include CH3S(O)2, CH3CH2S(O)2, CH3CH2CH2S(O)2, 35 (CH₃)₂CHS(O)₂ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers. "Alkenylthio" is defined analogously to the above examples.

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"Cycloalkyl" includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexyl and cycloctyl. "Cycloalkenyl" includes groups such as cyclopentenyl and cyclohexenyl as well as groups with more than one double bond such as 1,3- and 1,4-cyclohexadienyl.

"Tetrahydropyranyloxyalkynyl" denotes a tetrahydropyranyl group on oxygen which in turn is substituted on an alkynyl group. An example of "tetrahydropyranyloxyalkynyl" is 2-[(tetrahydro-2*H*-pyranyl)oxy]ethynyl.

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The term "aromatic carbocyclic ring system" includes fully aromatic carbocycles and carbocycles in which at least one ring of a polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied). The term "nonaromatic carbocyclic ring system" denotes fully saturated carbocycles as well as partially or fully unsaturated carbocycles where the Hückel rule is not satisfied by any of the rings in the ring system. The term "aromatic heterocyclic ring system" includes fully aromatic heterocycles and heterocycles in which at least one ring of a polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied). Examples of "aromatic heterocyclic ring systems" include furanyl, furazanyl, thienyl, pyrrolyl, pyrazolyl, oxazolyl, oxadiazolyl, imidazolyl, isoxazolyl, thiazolyl, thiadiazolyl, isothiazolyl, pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl and triazinyl with said ring attached through any available carbon or nitrogen. For example, when the aromatic heterocyclic ring is furanyl, it can be 2-furanyl or 3-furanyl, for pyrrolyl, the aromatic heterocyclic ring is 1-pyrrolyl, 2-pyrrolyl or 3-pyrrolyl, for pyridyl, the aromatic ring is 2-pyridyl, 3-pyridyl or 4-pyridyl and similarly for other aromatic heterocyclic rings. The term "nonaromatic heterocyclic ring system" denotes fully saturated heterocycles as well as partially or fully unsaturated heterocycles where the Hückel rule is not satisfied by any of the rings in the ring system. The heterocyclic ring systems can be attached through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen. One skilled in the art will appreciate that not all nitrogen containing heterocycles can form N-oxides since the nitrogen requires an available lone pair for oxidation to the oxide; one skilled in the art will recognize those nitrogen containing heterocycles which can form N-oxides.

The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. The term "1-2 halogen" indicates that one or two of the available positions for that substituent may be halogen which are independently selected. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F₃C, ClCH₂, CF₃CH₂ and CF₃CCl₂. The terms "haloalkenyl", "haloalkynyl", "haloalkoxy" and the like, are defined analogously to the term "haloalkyl". Examples of "haloalkenyl" include

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(Cl)₂C=CHCH₂ and CF₃CH₂CH=CHCH₂. Examples of "haloalkenyloxy" include (Cl)₂C=CHCH₂O and CF₃CH₂CH=CHCH₂O. Examples of "haloalkenylthio" include (Cl)₂C=CHCH₂S and CF₃CH₂CH=CHCH₂S. Examples of "haloalkynyl" include HC≡CCHCl, CF₃C≡C, CCl₃C≡C and FCH₂C≡CCH₂. Examples of "haloalkynyloxy" include CF₃C≡CCH₂O, CCl₃C≡CCH₂O and FCH₂C≡CCH₂O. Examples of "haloalkoxy" include CF₃O, CCl₃CH₂O, HCF₂CH₂CH₂O and CF₃CH₂O. Examples of "haloalkylthio" include CCl₃S, CF₃S, CCl₃CH₂S and ClCH₂CH₂CH₂S. Examples of "haloalkylsulfinyl" include CF₃S(O), CCl₃S(O), CF₃CH₂S(O) and CF₃CF₂S(O). Examples of "haloalkylsulfonyl" include CF₃S(O)₂, CCl₃S(O)₂, CF₃CH₂S(O)₂ and CF₃CF₂S(O)₂.

"Alkylcarbonyl" denotes alkyl substituted carbonyl. Examples of "alkylcarbonyl" include CH₃C(=O) and (CH₃)₂CHC(=O). "Alkoxycarbonyl denotes alkoxy substituted carbonyl. Examples of "alkoxycarbonyl" include CH₃OC(=O) and (CH₃)₂CHOC(=O). "Alkylcarbonylamino" denotes alkylcarbonyl substituted on nitrogen. Examples of "alkylcarbonylamino" include CH₃C(=O)NH and CH₃CH₂C(=O)NH. "Alkoxycarbonylamino" denotes alkoxycarbonyl substituted on nitrogen. Examples of "alkoxycarbonylamino" include CH₃OC(=O)NH and CH₃CH₂OC(=O)NH.

"Trialkylsilylalkoxyalkoxy" denotes trialkylsilyl substitution on alkoxy substituted in turn on alkoxy. Examples of "trialkylsilylalkoxyalkoxy" include (CH₃)₃SiCH₂OCH₂O and (CH₃)₃SiCH₂CH₂OCH₂O.

The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j are numbers from 1 to 10. For example, C₁-C₃ alkylsulfonyl designates methylsulfonyl through propylsulfonyl. Examples of "alkylcarbonyl" include CH₃C(=O), CH₃CH₂CH₂C(=O) and (CH₃)₂CHC(=O). Examples of "alkoxycarbonyl" include CH₃OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O), CH₃CH₂OC(=O) and the different butoxy- or pentoxycarbonyl isomers. In the above recitations, when a compound of Formula I is comprised of one or more heterocyclic rings, all substituents are attached to these rings through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen.

When a group contains a substituent which can be hydrogen, for example R⁹ or R¹³, then, when this substituent is taken as hydrogen, it is recognized that this is equivalent to said group being unsubstituted. When a group is optionally substituted with a substituent, for example with R⁷, then, when the group is not substituted with that substituent, it is recognized that this is equivalent to said group having a hydrogen substituent.

Compounds used in this invention often can exist as one or more stereoisomers.

The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be

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more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). (See, e.g., U.S. Provisional Patent Application Serial No. 60/057917 filed September 4, 1997, which is hereby incorporated by reference in its entirety.) Compounds of Formula II contain a chiral center. Enantiomers of Formula II with the S configuration (i.e., as defined by Cahn-Ingold-Prelog rules) are preferred. Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the present invention comprises compounds selected from Formula I, N-oxides and agriculturally suitable salts thereof. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

The salts of the compounds which may be used in the invention include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds which may be used in the invention also include those formed with organic bases (e.g., pyridine, ammonia, or triethylamine) or inorganic bases (e.g., hydrides, hydroxides, or carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group such as a phenol.

Preferred compositions for reasons of ease of synthesis or greater fungicidal activity are:

Preferred 1. A fungicidal composition comprising a fungicidally effective amount of (1) a compound of Formula I (including all geometric and stereoisomers), N-oxides, and agriculturally suitable salts thereof, wherein

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E is selected from the group 1,2-phenylene; 1,5-, 1,6-, 1,7-, 1,8-, 2,6-, 2,7-, 1,2-, and 2,3-naphthalenediyl; 1H-pyrrole-1,2-, 2,3- and 3,4-diyl; 2,3- and 3,4-furandiyl; 2,3- and 3,4-thiophenediyl; 1H-pyrazole-1,5-, 3,4- and 4,5-diyl; 1H-imidazole-1,2-, 4,5- and 1,5-diyl; 3,4- and 4,5-isoxazolediyl; 4,5-oxazolediyl; 3,4- and 4,5-isothiazolediyl; 4,5-thiazolediyl; 1H-1,2,3-triazole-1,5- and 4,5-diyl; 2H-1,2,3-triazole-4,5-diyl; 1H-1,2,4-triazole-1,5-diyl; 4H-1,2,4-triazole-3,4-diyl; 1,2,3-oxadiazole-4,5-diyl; 1,2,5-oxadiazole-3,4-diyl; 1,2,3-thiadiazole-4,5-diyl; 2,3- and 3,4-pyridinediyl; 3,4- and 4,5-pyridazinediyl; 4,5-pyrimidinediyl; 2,3-pyrazinediyl; 1,2,3-triazine-4,5-diyl; 1,2,4-triazine-5,6-diyl; 1H-indole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 1,2-, 2,3-, 4,5-, 5,6- and 6,7-benzofurandiyl;
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benzo[b]thiophene-2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 2,3-, 4,5-, 5,6- and 6,7-diyl; 1*H*-indazole-1,4-, 1,5-, 1,6-, 1,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 1H-benzimidazole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-diyl; 5 1,2-benzisoxazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-benzoxazolediyl; 1,2-benzisothiazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-benzothiazolediyl; 2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 2,3-, 3,4-, 5,6-, 10 6,7- and 7,8-quinolinediyl; 1,5-, 1,6-, 1,7-, 1,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and 7,8-isoquinolinediyl; 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and 7,8-cinnolinediyl; 1,5-, 1,6-, 1,7-, 1,8-, 5,6-, 6,7- and 7,8-phthalazinediyl; 2,5-, 2,6-, 2,7-, 2,8-, 4,5-, 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and 7,8-quinazolinediyl; 2,5-, 2,6-, 2,7-, 2,8-, 2,3-, 5,6-, 6,7-15 and 7,8-quinoxalinediyl; 1,8,-naphthyridine-2,5-, 2,6-, 2,7-, 3,5-, 3,6-, 4,5-, 2,3- and 3,4-diyl; 2,6-, 2,7-, 4,6-, 4,7-, 6,7-pteridinediyl; pyrazolo[5,1-b]thiazole-2,6-, 2,7-, 3,6-, 3,7-, 2,3- and 6,7-diyl; thiazolo[2,3-c]-1,2,4-triazole-2,5-, 2,6-, 5,6-diyl; 20 2-oxo-1,3-benzodioxole-4,5- and 5,6-diyl; 1.3-dioxo-1*H*-isoindole-2.4-, 2.5-, 4.5- and 5.6-divl: 2-oxo-2*H*-1-benzopyran-3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and 7,8-diyl; [1,2,4]triazolo[1,5-a]pyridine-2,5-, 2,6-, 2,7-, 2,8-, 5,6-, 6,7- and 7,8-diyl; 25 3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazine-3,5-, 3,6-, 3,7-, 3,8-, 5.6-, 6.7- and 7.8-diyl; 2.3-dihydro-2-oxo-3.4-, 3.5-, 3.6-, 3.7-, 4.5-, 5.6- and 6.7-benzofurandiyl; thieno[3.2-d]thiazole-2.5-, 2.6-, and 5,6-diyl; 5,6,7,8-tetrahydro-2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 2,3- and 3,4-quinolinediyl; 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazole-2,4-, 2,5-, 2,6-, 2,7-, 30 4,5-, 5,6- and 6,7-diyl; 1,3-benzodioxole-2,4-, 2,5-, 4,5- and 5,6-diyl; 2,3-dihydro-2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-benzofurandiyl; 2,3-dihydro-1,4-benzodioxin-2,5-, 2,6-, 2,7-, 2,8-, 5,6- and 6,7-diyl; and 35 5,6,7,8-tetrahydro-4H-cyclohepta[b]thiophene-2,4-, 2,5-, 2,6-, 2,7-, 2,8-, 3,4-, 3,5-, 3,6-, 3,7-, 3,8-, and 2,3-diyl; each aromatic ring system optionally substituted with one of R³, R⁴, or both R³ and R4;

W is O; R^1 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl; R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl or C₃-C₆ cycloalkyl; R³ and R⁴ are each independently halogen, cyano, nitro, C₁-C₆ alkyl, 5 C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfonyl, C₂-C₆ alkylcarbonyl, C₂-C₆ alkoxycarbonyl, (C₁-C₄ alkyl)NHC(O), (C₁-C₄ alkyl)₂NC(O), benzoyl or phenylsulfonyl; Y is -O-, $-S(O)_{n}$ -, $-NR^{15}$ -, -C(=O)-, $-CH(OR^{15})$ -, $-CH_{2}$ -, $-CH_{2}$ CH₂-, 10 -CH=CH-, -C \equiv C-, -CH₂O-, -OCH₂-, -CH₂S(O)_n-, -S(O)_nCH₂-, $-CH_2O-N=C(R^7)-$, $-(R^7)C=N-OCH(R^{15})-$, $-C(R^7)=N-O-$ or a direct bond: R⁷ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, C2-C6 alkenyl, C2-C6 alkynyl, C3-C6 cycloalkyl, halogen or cyano; 15 when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is -CH₂O-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as $-(CH_2)_r$ -J- such that J is attached to Z; Z is selected from the group C₁-C₁₀ alkyl; C₃-C₈ cycloalkyl; phenyl; naphthalenyl; anthracenyl; phenanthrenyl; 1H-pyrrolyl; furanyl; 20 thienyl; 1*H*-pyrazolyl; 1*H*-imidazolyl; isoxazolyl; oxazolyl; isothiazolyl; thiazolyl; 1*H*-1,2,3-triazolyl; 2*H*-1,2,3-triazolyl; 1H-1,2,4-triazolyl; 4H-1,2,4-triazolyl; 1,2,3-oxadiazolyl; 1,2,4-oxadiazolyl; 1,2,5-oxadiazolyl; 1,3,4-oxadiazolyl; 25 1,2,3-thiadiazolyl; 1,2,4-thiadiazolyl; 1,2,5-thiadiazolyl; 1,3,4-thiadiazolyl; 1*H*-tetrazolyl; 2*H*-tetrazolyl; pyridinyl; pyridazinyl; pyrimidinyl; pyrazinyl; 1,3,5-triazinyl; 1,2,4-triazinyl; 1,2,4,5-tetrazinyl; 1*H*-indolyl; benzofuranyl; benzo[*b*]thiophenyl; 1H-indazolyl; 1H-benzimidazolyl; benzoxazolyl; benzothiazolyl; 30 quinolinyl; isoquinolinyl; cinnolinyl; phthalazinyl; quinazolinyl; quinoxalinyl; 1,8-naphthyridinyl; pteridinyl; 2,3-dihydro-1*H*-indenyl; 1,2,3,4-tetrahydronaphthalenyl; 6,7,8,9-tetrahydro-5*H*-benzocycloheptenyl; 5,6,7,8,9,10-hexahydrobenzocyclooctenyl; 35 2,3-dihydro-3-oxobenzofuranyl; 1,3-dihydro-1-oxoisobenzofuranyl; 2,3-dihydro-2-oxobenzofuranyl; 3.4-dihydro-4-oxo-2*H*-1-benzopyranyl:

	3,4-dihydro-1-oxo-1 <i>H</i> -2-benzopyranyl;	
	3,4-dihydro-3-oxo-1 <i>H</i> -2-benzopyranyl;	
	3,4-dihydro-2-oxo-2H-1-benzopyranyl; 4-oxo-4H-1-benzopyranyl;	
	2-oxo-2 <i>H</i> -1-benzopyranyl;	
5	2,3,4,5-tetrahydro-5-oxo-1-benzoxepinyl;	
	2,3,4,5-tetrahydro-2-oxo-1-benzoxepinyl;	
	2,3-dihydro-1,3-dioxo-1 <i>H</i> -isoindolyl;	
	1,2,3,4-tetrahydro-1,3-dioxoisoquinolinyl;	
	3,4-dihydro-2,4-dioxo-2H-1,3-benzoxazinyl;	
10	2-oxo-1,3-benzodioxyl;	
	2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazolyl; 9H-fluorenyl;	
	azulenyl; and thiazolo $[2,3-c]-1,2,4$ -triazolyl; each group substituted	
	with R ⁹ and optionally substituted with one or more R ¹⁰ ;	
	R ¹⁵ is H, C ₁ -C ₃ alkyl or C ₃ -C ₆ cycloalkyl;	
15	and (2) at least one compound selected from compounds of (a)	
	Formula II, N-oxides and agriculturally suitable salts thereof,	
	and (b) bromuconazole, cyproconazole, difenoconazole, diniconazole,	
	epoxiconazole, fenarimol, fenbuconazole, fenpropidin,	
	fenpropimorph, fluquinconazole, flusilazole, flutriafol,	
20	hexaconazole, ipconazole, metconazole, penconazole, prochloraz,	
	propiconazole, tebuconazole, tetraconazole, triadimefon,	
	triadimenol, tridemorph, triticonazole and uniconazole.	
	Preferred 2. The fungicidal composition of Preferred 1 comprising a fungicidally	
	effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-	
25	(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-	
	triazol-3-one (sometimes referred to hereafter as the Formula Ia compound)	
	and (2) at least one compound selected from (a)	
	5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione	
	(sometimes referred to hereafter as the Formula IIa compound) and	
30	3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4H-	
	imidazol-4-one (sometimes referred to hereafter as the Formula IIb	
	compound) and (b) epoxiconazole, fenpropimorph, flusilazole,	
	propiconazole and tebuconazole.	
	Preferred 3. The fungicidal composition of Preferred 2 comprising a fungicidally	
35	effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-	
	(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-	
	triazol-3-one and (2) 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-	
	oxazolidinedione.	

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Preferred 4. The fungicidal composition of Preferred 2 comprising a fungicidally effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and (2) flusilazole.

- Preferred 5. The fungicidal composition of Preferred 2 comprising a fungicidally effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and (2) both 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione and flusilazole.
- The fungicidal compositions of this invention, in addition to comprising fungicidally effective amounts of the mixtures of the invention also optionally comprise at least one of a surfactant, a solid diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred component (1) and component (2) compounds.

This invention also relates to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of the mixtures of the invention (e.g., as a composition described herein). The preferred methods of use include those involving the above preferred compositions.

20 The Sterol Biosynthesis Inhibitor Fungicides

The class of sterol biosynthesis inhibitors includes DMI and non-DMI compounds, that control fungi by inhibiting enzymes in the sterol biosynthesis pathway. DMI fungicides have a common site of action within the fungal sterol biosynthesis pathway; that is, an inhibition of demethylation at position 14 of lanosterol or 24methylene dihydrolanosterol, which are precursors to sterols in fungi. Compounds acting at this site are often referred to as demethylase inhibitors, DMI fungicides, or DMIs. The demethylase enzyme is sometimes referred to by other names in the biochemical literature, including cytochrome P-450 (14DM). The demethylase enzyme is described in, for example, J. Biol. Chem. 1992, 267, 13175-79 and references cited therein. DMI fungicides fall into several classes: triazoles, imidazoles, pyrimidines, piperazines and pyridines. The triazoles includes bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, ipconazole, metconazole, penconazole, propiconazole, tebuconazole, tetraconazole, triadimenol, triadimenol, triticonazole and uniconazole. The imidazoles include clotrimazole, econazole, imazalil, isoconazole, miconazole and prochloraz. The pyrimidines include fenarimol, nuarimol and triarimol. The piperazines include triforine. The pyridines include buthiobate and pyrifenox. Biochemical investigations have shown that all of the above mentioned fungicides are

DMI fungicides as described by K. H. Kuck, et al. in *Modern Selective Fungicides - Properties, Applications and Mechanisms of Action*, Lyr, H., Ed.; Gustav Fischer Verlag: New York, 1995, 205-258.

The DMI fungicides have been grouped together to distinguish them from other sterol biosynthesis inhibitors, such as, the morpholine and piperidine fungicides. The morpholines and piperidines are also sterol biosynthesis inhibitors but have been shown to inhibit later steps in the sterol biosynthesis pathway. The morpholines include aldimorph, dodemorph, fenpropimorph, tridemorph and trimorphamide. The piperidines include fenpropidin. Biochemical investigations have shown that all of the above mentioned morpholine and piperidine fungicides are sterol biosynthesis inhibitor fungicides as described by K. H. Kuck, et al. in *Modern Selective Fungicides - Properties, Applications and Mechanisms of Action*, Lyr, H., Ed.; Gustav Fischer Verlag: New York, 1995, 185-204.

Synergistic Effects

Fungicides that effectively control plant fungi, such as wheat powdery mildew (Erysiphe graminis) and wheat glume blotch (Septoria nodorum), are in constant demand by growers. Combinations of fungicides are often used to facilitate disease control and to retard resistance development. Mixtures of fungicides may provide significantly better disease control than could be predicted based on the activity of the individual components. This synergism has been described as "the cooperative action of two components of a mixture, such that the total effect is greater or more prolonged than the sum of the effects of the two (or more) taken independently" (see Tames, P. M. L., Neth. J. Plant Pathology, (1964), 70, 73-80). It has been found that compositions containing the compound of Formula Ia and flusilazole and compositions containing the compounds of Formula Ia and Formula IIa exhibit synergistic effects.

The presence of a synergistic effect between two active ingredients is established with the aid of the Colby equation (see Colby, S. R. In *Calculating Synergistic and Antagonistic Responses of Herbicide Combinations*, Weeds, (1967), 15, 20-22):

$$p = A + B - \left[\frac{A \times B}{100} \right]$$

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Using the methods of the Colby, the presence of a synergistic interaction between two active ingredients is established by first calculating the predicted activity, p, of the mixture based on activities of the two components applied alone. If p is lower than the experimentally established effect, synergism has occurred. In the equation above, A is the fungicidal activity in percentage control of one component applied alone at rate x. The B term is the fungicidal activity in percentage control of the second component

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applied at rate y. The equation estimates p, the fungicidal activity of the mixture of A at rate x with B at rate y if their effects are strictly additive and no interaction has occurred.

In this application, fungicidal activities provided by compositions of Formula Ia, Formula IIa and flusilazole alone are compared with that of compositions of the compounds of Formula Ia and Formula IIa together and with that of compositions of the compounds of Formula Ia and flusilazole together. Based on the description of synergism developed by Colby, compositions of the present invention are considered to be synergistically useful. Accordingly, this invention provides an improved method of combating fungi, such as the control wheat powdery mildew (Erysiphe graminis) and the preventative control of wheat glume blotch (Septoria nodorum), in crops, especially cereals.

Compositions are provided in accordance with this invention which comprise proportions of component (1) and component (2) which are especially useful for controlling particular fungal diseases. For example, the compositions of this invention include those wherein the mole ratio of component (1) to component (2) is from about 15:1 to 1:15. Compositions including the compounds of Formula II are considered especially useful for controlling wheat powdery mildew (Erysiphe graminis) and compositions including the sterol biosynthesis inhibitor fungicides are considered especially useful for the preventative control of wheat glume blotch (Septoria nodorum). Preferred component (1) compounds for these compositions include 2,4-dihydro-5methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one. Preferred component (2) compounds for these compositions include 5-methyl-5-(4phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone; 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4H-imidazol-4-one; and flusilazole. Preferably, the mole ratio of component (1) to component (2) for these compositions is from about 4:1 to 1:15. Example compositions of this type include compositions comprising 2,4dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one and 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone in a mole ratio of the compound of Formula Ia to the compound of Formula IIa of from about 4:1 to 1:4; and compositions comprising 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one and flusilazole in a mole ratio of the compound of Formula Ia to flusilazole of about 4:1 to 1:15.

This invention also provides processes for the control of wheat powdery mildew and the preventative control of wheat glume blotch which comprises applying to the

plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 15:1 to 1:15 (preferably from about 4:1 to 1:15). Component (1) can, for example, be applied at a rate of 0.2 g/ha or more. Typically component (1) is applied at a rate of 125 g/ha. Component (2) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

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Compositions wherein component (2) is selected from the group consisting of compounds of Formula II; and wherein the mole ratio of component (1) to component (2) is from about 15:1 to 1:15 are considered especially useful for controlling wheat powdery mildew. Preferred component (1) compounds for these compositions include 2.4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

15 (trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one. Preferred component (2) compounds for these compositions include 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone and 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4*H*-imidazol-4-one; with 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone being particularly preferred.

Preferably, the mole ratio of component (1) to component (2) for these compositions is from about 4:1 to 1:4. Example compositions of this type include compositions comprising 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone in a mole ratio of

the compound of Formula Ia to the compound of Formula IIa of from about 4:1 to 1:4.

This invention also provides a process for controlling wheat powdery mildew which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 4:1 to 1:4. Component (1) can, for example, be applied at a rate of 0.2 g/ha or more. Typically component (1) is applied at a rate of 125 g/ha. Component (2) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

Compositions wherein component (2) is selected from the group consisting of 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinone; 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4*H*-imidazol-4-one;

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flusilazole; epoxiconazole; fenpropimorph; propiconazole; and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from about 15:1 to 1:15 are considered especially useful for the preventative control of wheat glume blotch. Preferred component (1) compounds for these compositions include 2,4-dihydro-5methoxy-2-methyl-4-[2-[[[1-[3-5 (trifluoromethyl)phenyllethylidenelaminoloxylmethyllphenyll-3H-1,2,4-triazol-3-one. Preferred component (2) compounds for these compositions include sterol biosynthesis inhibitor fungicides; with epoxiconazole, flusilazole, propiconazole and tebuconazole being particularly preferred. Preferably, the mole ratio of component (1) to component (2) for these compositions is from about 4:1 to 1:15. Example compositions of this type 10 include compositions comprising 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one and flusilazole in a mole ratio of the compound of Formula Ia to flusilazole of from about 4:1 to 1:15.

This invention also provides a process for the preventative control of wheat glume blotch, which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 4:1 to 1:15. Component (1) can, for example, be applied at a rate of 5 g/ha or more. Typically component (1) is applied at a rate of 125 g/ha. Component (2) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

25 Synthesis of Compounds of Formula I

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The compounds of Formula I can be prepared by one or more of the following methods and variations as described in Schemes 1-2 and International Patent Application WO 95/14009. The definitions of A, E, G, W, X, Y, Z, R¹ and R²in the compounds of Formulae 1-5 below are as defined above in the Summary of the Invention. The compound of Formula Ia is a subset of the compounds of Formula I.

Compounds of Formula I can be prepared as described in International Patent Application WO 95/14009. A synthesis of the compounds of Formula I involves treating a compound of Formula 1 with an appropriate alkyl transfer reagent in an inert solvent with or without additional acidic or basic reagents or other reagents (Scheme 1). Suitable solvents are selected from the group consisting of polar aprotic solvents such as acetonitrile, dimethylformamide or dimethylsulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; and halocarbons such as dichloromethane or chloroform.

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Scheme 1

Method 1: V-CH=
$$N_2$$
 (V = H or (CH₃)₃Si)

Method 4:
$$(CH_3)_2SO_4$$
; R^1OSO_2V ; or CH_3 -hal; optional base
(hal = F, Cl, Br, or I)
 $(V = C_1 - C_6 \text{ alkyl}, C_1 - C_6 \text{ haloalkyl})$

For example, compounds of Formula I can be prepared by the action of diazoalkane reagents of Formula 2 such as diazomethane (V = H) or trimethylsilyldiazomethane ($V = (CH_3)_3Si$) on compounds of Formula 1 (Method 1). Use of trimethylsilyldiazomethane requires a protic cosolvent such as methanol. For examples of these procedures, see *Chem. Pharm. Bull.*, (1984), 32, 3759.

As indicated in Method 2, compounds of Formula I can also be prepared by contacting carbonyl a compound of Formula 1 with alkyl trichloroacetimidates of Formula 3 and a Lewis acid catalyst. Suitable Lewis acids include trimethylsilyl triflate and tetrafluoroboric acid. The alkyl trichloroacetimidates can be prepared from the appropriate alcohol and trichloroacetonitrile as described in the literature (J. Danklmaier and H. Hönig, *Synth. Commun.*, (1990), 20, 203).

Compound of Formula I can also be prepared from compounds of Formula 1 by treatment with a trialkyloxonium tetrafluoroborate (i.e., Meerwein's salt) of Formula 4 (Method 3). The use of trialkyloxonium salts as powerful alkylating agents is well known in the art (see U. Schöllkopf, U. Groth, C. Deng, *Angew. Chem., Int. Ed. Engl.*, (1981), 20, 798).

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Other alkylating agents which can convert compounds of Formula 1 to compounds of Formula I are dialkyl sulfates such as dimethyl sulfate, haloalkyl sulfonates such as methyl trifluoromethanesulfonate, and alkyl halides such as iodomethane and propargyl bromide (Method 4). These alkylations can be conducted with or without additional base. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, or tertiary amines such as triethylamine, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylenediamine. See R. E. Benson, T. L. Cairns, J. Am. Chem. Soc., (1948), 70, 2115 for alkylation examples using agents of this type.

Compounds of Formula I, where A, G, E, W, X, Y, Z, R¹ and R² are defined as above, can also be prepared by reaction of Formula 5 compounds with alkali metal alkoxides (R¹O-M⁺) (Scheme 2). The leaving group Lg¹ in the amides of Formula 5 are any group known in the art to undergo a displacement reaction of this type. Examples of suitable leaving groups include chlorine, bromine, and sulfonyl and sulfonate groups. Examples of suitable inert solvents are dimethylformamide or dimethylsulfoxide.

Scheme 2

 $Lg^1 = Cl$, Br, $-SO_2V$, or $-OSO_2V$ $V = C_1-C_6$ alkyl or C_1-C_6 haloalkyl M = K or Na

2,4-Dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, Formula Ia, is a compound of Formula I where E is 1,2-phenylene, A is N, G is N with the floating double bond attached to A, W is O, X is OR¹, R¹ is CH₃, R² is CH₃, Y is -CHR¹⁵O-N=C(R⁷)-, R⁷ is CH₃, R¹⁵ is H, Z is phenyl substituted with R⁹ and R⁹ is CF₃ fixed in the 3 position.

Synthesis of Compounds of Formula II

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The compounds of Formula II can be prepared by one or more of the following methods and variations as described in Scheme 3, International Patent Application WO 94/11359 and European Patent Application EP-A-551048. The compounds of Formulae II and IIb are various subsets of the compounds of Formula II.

The compound of Formula IIa (where E¹ is -OC(=O)CH₂- and R²⁸ is phenoxy)

can be prepared as depicted in Scheme 3 and described in International Patent

Application WO 94/11359.

Scheme 3

$$CH_3$$
 OH OR^{29} $OR^{$

wherein:

R²⁹ is C₁-C₄ alkyl; and

Lg¹ is 1-imidazolyl or 1,2,4-triazolyl

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Reaction conditions suitable for preparing the compound of Formula IIa are as follows. For the conversion of esters of Formula 6 to compounds of Formula 8, the suitable solvents include inert organic solvents. Preferred solvents are methylene chloride, chloroform, carbon tetrachloride, hexanes, tetrahydrofuran, *tert*-butyl methyl ether, dioxanes, chlorobenzene, *o*-dichlorobenzene (ODCB), toluene, xylenes, and suitable combinations thereof. The most preferred solvents are selected from the group consisting of chlorobenzene, ODCB, toluene, and xylenes. The reaction temperatures can range from about 10°C to about 75°C. Preferred temperatures are from about 40°C to about 60°C. Suitable reaction pressures are from about 1.0 x 10⁵ to about 5.1 x 10⁵ Pascals. The preferred pressure is 1 x 10⁵ Pascals. The reaction times are typically 1 to 24 hours, preferably 3 to 6 hours. A suitable ratio of Formula 7 to 6 is from about 1:1 to 2:1. The preferred ratio is from about 1.1:1 to 1.8:1. Suitable bases for this reaction include trialkylamines, imidazole, pyridine, picolines or other substituted pyridine derivatives.

For the conversion of compounds of Formula 8 to the 2,4-oxazolidinedione of Formula IIa, suitable solvents are as noted above for the condensation of Formulae 6 and 7. The preferred solvents are those disclosed above as preferred. The reaction temperatures are from about 0°C to about 75°C. Preferred temperatures are from about 10°C to about 50°C. Reaction pressures are from about 1.0 x 10⁵ to about 5.1 x 10⁵ Pascals. The preferred pressure is 1 x 10⁵ Pascals. The reaction times are typically 1 to 24 hours, preferably 2 to 6 hours. The acids suitable for catalyzing the reaction are selected from the group consisting of alkyl and aryl carboxylic acids, trialkylammonium halides and combinations thereof. The preferred acids are acetic acid and triethylammonium chloride. The most preferred acid is triethylammonium chloride. Suitable ratios of phenylhydrazine to Formula 8 is from about 2:1 to 1:1. The preferred ratio is from about 1.6:1 to 1.1:1.

The carbonylating agent of Formula 7 may be added as a pure compound, a solution of the pure compound in an inert solvent, or prepared in situ in the presence of the ester of Formula 6. The preferred process involves preparation of the carbonylating agent in situ.

Methods for preparing compounds of Formula 7, including in situ methods, from phosgene [or phosgene equivalents such as diphosgene (trichloromethyl chloroformate) or triphosgene (bis(trichloromethyl)carbonate)] and either imidazole or triazole are known in the art (see *Org. Syntheses*. Coll. Vol. 5, 201, (1973)). Reactions wherein HCl is liberated require a base to trap the acid. A suitable base is a trialkylamine or imidazole, or combinations thereof. The preferred base is triethylamine.

1,1'-Carbonylditriazole (Formula 7 wherein Lg¹ = 1,2,4-triazolyl) can also be prepared by treating a metal alkali salt of triazole, preferably the potassium salt, with phosgene

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(or phosgene equivalent) in a solvent. Phase transfer catalysts are preferably added to reactions wherein the triazole salt has low solubility in the solvent. For example, phase transfer catalysts are preferred when xylenes or toluene is used. Any phase transfer catalyst known to one skilled in the art is suitable. Tetraalkylammonium halides are preferred. The triazole salt is prepared by treating triazole with a suitable base, such as sodium hydroxide or sodium ethoxide. The preferred relative amount of alkali metal base to triazole to phosgene is 0.5:1.0:0.6.

Base is also necessary to catalyze the condensation of Formulae 6 and 7. As previously stated, suitable base catalysts are trialkylamines, imidazole, pyridine, picolines or other substituted pyridines. When 1,1'-carbonyldiimidazole is used (Formula 7 wherein Y=1-imidazolyl), the imidazole which is liberated upon reaction with Formula 6 serves as the catalyst. When 1,1'-carbonylditriazole is used, the preferred base is pyridine, a picoline, or a mixture of picoline isomers.

Compounds of Formula 8 may be isolated and purified, or treated in situ with phenylhydrazine and acid to form the 2,4-oxazolidinedione of Formula IIa. The preferred method involves treatment of Formula 8 in situ with phenylhydrazine. After the formation of the carbamate of Formula 8 is complete, excess carbonylating agent can be decomposed by the addition of water.

The compound of Formula IIb (where E¹ is -N=C(SCH₃)CH₂- and R²⁸ is H) can be prepared as described in European Patent Application EP-A-551048.

Пb

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Percentages are by weight except for chromatographic solvent mixtures or where otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated.

1 H NMR spectra are reported in ppm downfield from tetramethylsilane; s = singlet, d = doublet and m = multiplet.

EXAMPLE 1

<u>Preparation of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one</u>

5 A 100 mL 1-necked round bottom flask is fitted with a magnetic stirrer and reflux condenser capped with a nitrogen bypass. The flask is charged with 50 mL of tetrahydrofuran, 2.12 g of 5-chloro-2,4-dihydro-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]-ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one (5 mmol) and 1.19 g of 25% sodium methoxide in methanol (5.5 mmol). The mixture is 10 heated to reflux with stirring. After 4 h, 0.10 g of 25% sodium methoxide in methanol is added. After an additional 2 h, 0.30 g of 25% sodium methoxide in methanol is added. The mixture is then stirred at reflux for one additional hour at which time analysis of an aliquot by high pressure liquid chromatography indicates the presence of essentially no starting material. The mixture is allowed to cool to room temperature and left stirring overnight. The mixture is then worked up as in Example 3 to yield 2.06 g of pale yellow oil which crystallized upon seeding with an authentic sample of 2,4dihydro-5-methoxy-2-methyl-4-[2[[[[1-[3-(trifluoromethyl)phenylethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one. Trituration with hexanes followed by filtration and drying gave 1.97 g of white solid, m.p. 97-98.5°C. A portion (1.00 g) of this was recrystallized from 10 mL of 10% ethyl acetate-hexane to yield 20 0.94 g of white solid, m.p. 101-102°C. H¹NMR (CDCl₃) δ 2.21 (s,3H), 3.40 (s,3H), 3.89 (s,3H), 5.24 (d,2H), 5.28 (d,2H), 7.26 (m,1H), 7.47 (m,3H), 7.58 (m,2H), 7.85 (m,2H).

Formulation/Utility

- 25. The fungicidal compositions of the present invention comprise an effective amount of a mixture of the compounds(s) of component (1) (e.g., 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one) and the compound(s) of component (2) (e.g.,
- 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione;
 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4H-imidazol-4-one;
 epoxiconazole, fenpropimorph, flusilazole; propiconazole and/or tebuconazole). The mixtures of this invention will typically be used as a formulation or composition with an agriculturally suitable carrier comprising at least one of a liquid diluent, a solid diluent or a surfactant. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Useful formulations

include liquids such as solutions (including emulsifiable concentrates), suspensions,

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emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wettable") or water-soluble. Active ingredient can be

[micro]encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredients, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

•		Weight Percent	
_	Active Ingredients	<u>Diluent</u>	Surfactant
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5–90	0–94	1–15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5–50	40–95	0–15
Dusts	1–25	70 -99	0–5
Granules and Pellets	0.01 -99	5–99.99	0–15
High Strength Compositions	90-99	0-10	0–2

Typical solid diluents are described in Watkins, et al., Handbook of Insecticide Dust Diluents and Carriers, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, Solvents Guide, 2nd Ed., Interscience, New York, 1950. McCutcheon's Detergents and Emulsifiers Annual, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, Encyclopedia of Surface Active Agents, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N*,*N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar,

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silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N*,*N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkylnaphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding as in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. Patent No. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", Chemical Engineering,

- December 4, 1967, pp 147-48, Perry's Chemical Engineer's Handbook, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and International Patent Publication WO 91/13546. Pellets can be prepared as described in U.S. Patent No. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. Patent No. 4,144,050, U.S. Patent No. 3,920,442 and
- German Patent Publication DE 3,246,493. Tablets can be prepared as taught in U.S. Patent No. 5,180,587, U.S. Patent No. 5,232,701 and U.S. Patent No. 5,208,030. Films can be prepared as taught in Great Britain Patent Publication GB 2,095,558 and U.S. Patent No. 3,299,566.

For further information regarding the art of formulation, see

- U.S. Patent No. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41;
 U.S. Patent No. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182;
 U.S. Patent No. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4;
 Klingman, Weed Control as a Science, John Wiley and Sons, Inc., New York, 1961,
 pp 81-96; and Hance et al. Weed Control Handbook, 8th Ed. Blackwell Scientific
- 30 pp 81-96; and Hance et al., Weed Control Handbook, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways.

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Example	A

	Example A	
<u>V</u>	Vettable Powder	
	Active ingredient(s)	65.0%
	dodecylphenol polyethylene glycol ether	2.0%
5	sodium ligninsulfonate	4.0%
	sodium silicoaluminate	6.0%
	montmorillonite (calcined)	23.0%.
	Example B	
<u>G</u>	ranule	
0	Active ingredient(s)	10.0%
	attapulgite granules (low volatile matter,	•
	0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.
	Example C	
E	xtruded Pellet	
;	Active ingredient(s)	25.0%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
	sodium alkylnaphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.
0	Example D	
E	Emulsifiable Concentrate	
	Active ingredient(s)	20.0%
	blend of oil soluble sulfonates	
	and polyoxyethylene ethers	10.0%
5	isophorone	70.0%.
		. •

The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete and Deuteromycete classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola*, *Phytophthora infestans*, *Peronospora tabacina*, *Pseudoperonospora cubensis*, *Pythium aphanidermatum*, *Alternaria brassicae*, *Septoria nodorum*, *Septoria tritici*, *Cercosporidium personatum*, *Cercospora arachidicola*, *Pseudocercosporella herpotrichoides*, *Cercospora beticola*,

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Botrytis cinerea, Monilinia fructicola, Pyricularia oryzae, Podosphaera leucotricha, Venturia inaequalis, Erysiphe graminis, Uncinula necatur, Puccinia recondita, Puccinia graminis, Hemileia vastatrix, Puccinia striiformis, Puccinia arachidis. Rhizoctonia solani, Sphaerotheca fuliginea, Fusarium oxysporum, Verticillium dahliae, Pythium aphanidermatum, Phytophthora megasperma, Sclerotinia sclerotiorum, Sclerotium rolfsii, Erysiphe polygoni, Pyrenophora teres, Gaeumannomyces graminis, Rynchosporium secalis, Fusarium roseum, Bremia lactucae and other generea and species closely related to these pathogens.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of such agricultural protectants with which compounds of this invention can be formulated are: insecticides such as abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorfenapyr, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flucythrinate, tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methyl 7-chloro-20 2,5-dihydro-2-[[N-(methoxycarbonyl)-N-[4-(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2-e][1,3,4]oxadiazine-4a(3H)carboxylate (DPX-JW062), monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, 25 tralomethrin, trichlorfon and triflumuron; fungicides such as azoxystrobin, benomyl, blasticidin-S, Bordeaux mixture (tribasic copper sulfate), captafol, captan, carbendazim, chloroneb, chlorothalonil, copper oxychloride, copper salts, cymoxanil, cyprodinil (CGA 219417), diclomezine, dicloran, dimethomorph, dodine, edifenphos, famoxadone, fenpiclonil, fluazinam, flutolanil, folpet, fosetyl-aluminum, furalaxyl, iprobenfos, 30 iprodione, isoprothiolane, kasugamycin, kresoxim-methyl, mancozeb, maneb, mepronil, metalaxyl, (E)-2-(methoxyimino)-N-methyl-2-(2-phenoxyphenyl)acetamide (SSF 126), S-methyl 7-benzothiazolecarbothioate (CGA 245704), myclobutanil, neo-asozin (ferric methanearsonate), oxadixyl, pencycuron, probenazole, prochloraz, pyrifenox, pyroquilon, quinoxyfen, spiroxamine (KWG4168), sulfur, thiabendazole, 35 thiophanate-methyl, thiram, tricyclazole, validamycin and vinclozolin; nematocides such as aldoxycarb and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, etoxazole,

fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite, pyridaben and tebufenpyrad; and biological agents such as *Bacillus thuringiensis*, *Bacillus thuringiensis* delta endotoxin, baculovirus, and entomopathogenic bacteria, virus and fungi.

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In certain instances, combinations with other fungicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this invention either pre- or post-infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied to the seed to protect the seed and seedling.

Rates of application for this composition can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of aggregate active ingredient. Aggregate active ingredient is defined as the total combined weight of active ingredients. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g of aggregate active ingredient per kilogram of seed.

The following Examples demonstrate the composition and method of the present invention and provide experimental evidence for synergy between the compound of Formula Ia and flusilazole in preventative control of wheat glume blotch caused by *Septoria nodorum*. The experimental also provides evidence for synergy between the compound of Formula Ia and IIa in preventative and curative control of wheat powdery mildew caused by *Erysiphe graminis*. The experimental also provides evidence for synergy between the compound of Formula Ia and IIa in preventative and curative control of grape downy mildew caused by *Plasmopara viticola*.

The following TESTS demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the compounds is not limited, however, to these species.

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BIOLOGICAL EXAMPLES OF THE INVENTION

Test compounds were first dissolved in acetone in an amount equal to 50% of the final volume and then suspended at a concentrations from 0.08 to 200 ppm in purified water containing 250 ppm of the surfactant Trem® 014 (polyhydric alcohol esters).

5 The resulting test suspensions were then used in the following test protocols. Spraying these test suspensions to the point of run-off on the test plants is the equivalent of a rate of 500 g/ha.

Protocol #1 - WPM Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. tritici, (the causal agent of wheat powdery mildew). Seedlings were incubated in a growth chamber at 20°C for 6 days, after which disease ratings were made.

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Protocol #2 - WPM Curative

Wheat seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. tritici, (the causal agent of wheat powdery mildew). The following day a test compounds were sprayed to the point of run-off on and seedlings incubated in a growthchamber at 20°C for 7 days, after which disease ratings were made.

Protocol #3 WLR Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia* recondita (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

Protocol #4 - WLR Curative

Wheat seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust). The following day the test compounds were sprayed to the point of run-off on and incubated in a saturated atmosphere at 20°C for 24 h, then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

Protocol #5 - WFR Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Pseudocercosporella herpotrichoides* (the causal agent of wheat eye spot or wheat foot rot) and incubated in a saturated atmosphere at 20°C for 72 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

Protocol #6 - WGB Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Septoria* nodorum (the causal agent of wheat glume blotch) and incubated in a saturated atmosphere at 20°C for 48 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

Protocol #7 - WGB Curative

Wheat seedlings were inoculated with a spore suspension Septoria nodorum (the causal agent of wheat glume blotch). Two days later test compounds were sprayed to the point of run-off on and seedlings incubated in a saturated atmosphere at 20°C for 48 h, then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

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Protocol #8 - RCB Curative

Wheat seedlings were inoculated with a spore suspension *Pyricularia oryzae* (the causal agent of rice Blast). The following day test compounds were sprayed to the point of run-off on and seedlings incubated in a saturated atmosphere at 20°C for 48 h, then moved to greenhouse at 27°C for 8 days, after which disease ratings were made.

Protocol #9 - RSB Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Rizoctonia* solani (the causal agent of rice sheath blight) and incubated in a saturated atmosphere at 20°C for 48 h, and then moved to a greenhouse at 27°C for 8 days, after which disease ratings were made.

Protocol # 10 - PLB Preventive

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora* infestans (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

Protocol # 11 - PLB Curative

Wheat seedlings were inoculated with a spore *Phytophthora infestans* (the causal agent of potato and tomato late blight). The following day test compounds were sprayed to the point of run-off on and seedlings incubated in a saturated atmosphere at 20°C for 48 h, then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

Protocol # 12 - GDM Preventive

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Plasmopara* viticola (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

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Protocol # 13 - GDM Curative

Wheat seedlings were inoculated with a spore *Plasmopara viticola* (the causal agent of grape downy mildew). The following day test compounds were sprayed to the point of run-off on and seedlings incubated in a saturated atmosphere at 20°C for 48 h, then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

Results for protocols 1 - 13 are given in Tables A-F. In the tables, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). An (nt) indicates no test results and (-) indicates no estimate of activity. In Tables A-F rates are given in parts per million (ppm) and/or grams active ingredient per hectare (g a.i./ha). The term "Actual" stands for the experimental value. The abbreviation "Exp." stands for "Expected" (i.e., the predicted activity, p, from the Colby equation).

TABLEA

Synergistic Effects of Compound Ia / Flusilazole Combinations for Preventive Control of Wheat Powdery Mildew (WPM), Wheat Leaf Rust (WLR), Wheat Foot Rot (WFR) and Wheat Glume Blotch (WGB)

	€	Exp.	ŀ	ł	:	1	i	80.2	98.9	99.3	99.5	100	100
	WGB ⁽⁴⁾	<u>Actual</u>	49	66	45	26	86	93	66	66	26	93	66
<u>19</u>	<u>@</u>	Exp.	i	ı	i,	;	ì	65.1	100	100	92.9	100	100
Percent Disease Control	WFR ⁽³⁾	Actual	17	83	28	100	100	52	100	100	54	100	100
cent Dise	(S)			ŀ									
Per	WLR ⁽²⁾	Actual	66	66	0	00 00	100	66	86	26	86	66	100
		Exp.	ł	;	ŀ	ŧ	ł	9.66	266	100	100	100	100
	WPM ⁽¹⁾	Actual	96	100	68	35	100	66	66	100	66	66	100
	Mole	Ratio	٠					1:1.5	3.33:1	13.33:1	1:7.5	1:1.5	2.67:1
	Rate	(g a.i./ha)	\$	10 25	2.5	12.5	20	2.5 + 5	12.5 + 5	50+5	2.5 + 25	12.5 + 25	50 + 25
	Rate	(mdd)	7	10	-	5	20	1+2	5+2	20 + 2	1 + 10	5 + 10	20 + 10
• •	Test	Cmpd 2	:	;	ł	ŀ	ŀ	Ia	Ia	Ia	Ia	Ia	Ia
	Test	Cmpd 1	Ia	Ia	Flusilazole								

(1) Wheat powdery mildew activity - Protocol #1

⁽²⁾ Wheat leaf rust activity - Protocol #3

⁽³⁾ Wheat foot rot activity - Protocol # 5

⁽⁴⁾ Wheat glume blotch activity - Protocol # 6

Synergistic Effects of Compound Ia / Compound IIa Combinations for Preventive Control of Wheat Powdery Mildew (WPM), TABLEB

Wheat Leaf Rust (WLR), Wheat Foot Rot (WFR) and Wheat Glume Blotch (WGB)

	B(4)	Exp.	ı	ı	:	:	ı	ı	12	32	96.1
	WGB ⁽⁴⁾										
[o]	<u></u>	Exp.	ı	1	ì	:	:	1	0	12	89
Percent Disease Control	$\overline{\mathrm{WFR}^{(3)}}$	Actual	0	0	0	0	12	59	0	0	12
ent Dise	[2]	Exp.	;	:	ŀ	1	:	:	81.3	66	9.66
Perc	WLR ⁽²⁾	<u>Actual</u>	15	65	64	78	24	66	51	94	86
	ĘĮ	Exp.	į	ŧ	i	ł	ŀ	ł	40.2	26	100
	WPN	Actual	S	0	0	37	26	100	55	26	100
	Mole	Ratio							1:1.13	1:1.13	1:1.13
	Rate	(g a.i./ha)	0.2	-	8	0.2	-	8	0.2 +0.2	1+1	5+5
	Rate	(mdd)	0.08	4.0	2	0.08	9.4	2	0.08 + 0.08	0.4 + 0.4	2+2
	Test	Cmpd 2	;	;	i	1	:	:	Ia	Ia	Ia
	Test	Cmpd 1	IIa	IIa	IIa	Ia	Ia	Ia	IIa	IIa	IIa

(1) Wheat powdery mildew activity - Protocol #1

(4) Wheat glume blotch activity - Protocol # 6

⁽²⁾ Wheat leaf rust activity - Protocol #3

⁽³⁾ Wheat foot rot activity - Protocol # 5

Synergistic Effects of Compound Ia / Flusilazole Combinations for Curative Control of Wheat Powdery Mildew (WPM), Wheat Leaf Rust (WLR) and Wheat Glume Blotch (WGB) TABLEC

						•	Percent Disease Contro	se Control		
Test	Test	Rate	Rate	Mole	WPM ⁽¹⁾	M(I)	WLR ⁽²⁾	R ⁽²⁾	WGB ⁽³⁾	<u>@</u>
Cmpd 1	Cmpd 2	(mdd)	(g a.i./ha)	Ratio	Actual	Exp.	Actual	Exp.	<u>Actual</u>	Exp.
Ia	:	7	5		100	ŀ	79	;	20	1
Ia i	ŀ	10	25		100	ł	100	;	93	ı
Flusilazole	ŀ	-	2.5		78	ŀ	22	:	10	I
Flusilazole	:	\$	12.5		66	ı	26	i	10	ł
Flusilazole	;	20	20		100	ŀ	100	;	89	:
Flusilazole	Ia	1+2	2.5 + 5	1:1.5	89	100	<i>L</i> 9	83.6	70	55
Flusilazole	Ia	5+2	12.5 + 5	3.33:1	66	100	100	99.4	80	55
Flusilazole	Ia	20+2	50 + 5	13.33:1	100	100	100	100	84	84
Flusilazole	ľa	1+10	2.5 + 25	1:7.5	89	100	<i>L</i> 9	100	99	100
Flusilazole	Ia	5 + 10	12.5 + 25	1:1.5	66	100	100	100	29	100
Flusilazole	Ia	20 + 10	20+10 50+25	2.67:1	100	100	100	100	83	100

(1) Wheat powdery mildew activity - Protocol #2

⁽²⁾ Wheat leaf rust activity - Protocol #4

⁽³⁾ Wheat glume blotch activity - Protocol #7

Synergistic Effects of Compound Ia / Compound IIa Combinations for Curative Control of Wheat Powdery Mildew (WPM), TABLED

Wheat Leaf Rust (WLR) and Wheat Glume Blotch (WGB)

	B (3)	Exp	•1	;	ı	ŀ	:	ŀ	:	0	0	0
	WGB ⁽³⁾	Actual		0	0	0	0	0	0	0	0	0
Percent Disease Control	R ⁽²⁾	Exp.		1	1	ŀ	:	1	ı	0	0	0
rcent Dise	WLR ⁽²⁾	Actual		0	0	0	0	0	0	0	0	78
Pe	WPM ⁽¹⁾	Exp.		ŀ	ŧ	:	1	;	:	0	35	97.1
	WP	Actual Exp.		0	0	64	0	35	95	73	80	66
		Ratio								1:1.13	1:1.13	1:1.13
	Rate	(g a.i./ha)			П	5	0.2		5	0.2 + 0.2	1+1	5+5
	Rate	(mdd)		0.08	0.4	2	0.08	4.0	2	0.08 + 0.08	0.4 + 0.4	2+2
	Test	Cmpd 2		i	;	ŀ	ŀ	:	;	Ia	ľa	Ia
	Test	Cmpd 1		IIa	IIa	IIa	la	ľa	Ia	IIa	IIa	IIa

(1) Wheat powdery mildew activity - Protocol #2

(3) Wheat glume blotch activity - Protocol # 7

⁽²⁾ Wheat leaf rust activity - Protocol # 4

TABLE E

Synergistic Effects of Compound Ia / Compound IIa Combinations for Preventive Control of Rice Blast (RCB), Rice Sheath Blight (RCB), Potato Late Blight (PLB) and Grape Downy Mildew (GDM)

	E	Exp.	:	:	ł	:	;	1	47	61.8	100
				43							
킮	୍ଥା	Exp.	ŀ	:	:	;	:	:	0	0	17
ase Contr	FLI	Actual	0	0	17	0	0	0	0	0	17
ercent Dise	<u>@</u>	Exp.	1	ı	i	ŀ	ı	:	0	0	0
Fer	RSE	Actual	0	0	0	0	0	0	0	0	28
	() ()	Exp.	i	ŀ	ŀ	ŀ	;	}	0	0	Π
	RC.	Actual Exp.	0	0	0	0	0	11	0	0	0
		Ratio								1:1.13	
	Rate	(g a.i./ha)	0.2	-	ς.	0.2		ς,	0.2 + 0.2	1+1	5+5
	Rate	(mdd)	80.0	0.4	7	0.08	0.4	7	0.08 ± 0.08	0.4 + 0.4	2+5
				:							
	Test	Cmpd 1	IIa	IIa	IIa	Ia	Ia	Ia	IIa	IIa	IIa

(1) Rice blast - Protocol #8

⁽²⁾ Rice sheath blight - Protocol # 9

⁽³⁾ Potato late blight - Protocol # 10

⁽⁴⁾ Grape downy mildew - Protocol # 12

Synergistic Effects of Compound Ia / Compound IIa Combinations for Curative Control of Rice Blast (RCB), Rice Sheath Blight (RCB), Potato Late Blight (PLB) and Grape Downy Mildew (GDM) TABLEF

	ତ୍ରା	Exp.	ł	i	ì	;	ł	1	0	0	0
	GDW ⁽³⁾	Actual	0	0	0	0	0	0	0	16	76
Percent Disease Control	PLB ⁽²⁾	Exp.	ł								
Percent Dise	II.	<u>Actual</u>	0	0	0	0	0	0	0	0	0
	<u> </u>		:	;	;	1	ì	;	0	0	0
	RCB ⁽¹⁾	<u>Actual</u>	0	0	0	0	0	0	0	0	0
	Mole	Ratio							1:1.13	1:1.13	1:1.13
	Rate	(g a.i./ha)	0.2	-	5	0.2	-	ν,	0.2 +0.2	1+1	5+5
	Rate	(mdd)	0.08	0.4	2	0.08	0.4	7	0.08 ± 0.08	0.4 + 0.4	2+2
	Test	Cmpd 2	:	ł	;	:	ŀ	:	Ia	Ia	Ia
	Test	Cmpd 1	IIa	IIa	IIa	Ia	Ia	Ia	IIa	IIa	IIa

(1) Rice blast - Protocol #8

⁽²⁾ Potato late blight - Protocol # 11

⁽³⁾ Grape downy mildew - Protocol # 13

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CLAIMS

What is claimed is:

- A fungicidal composition comprising:
- (1) at least one compound selected from the compounds of Formula I, N-oxides
 and agriculturally suitable salts thereof,

wherein

E is selected from:

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i) 1,2-phenylene optionally substituted with R³ or both R³ and R⁴; ii) naphthalenediyl, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalenediyl optionally substituted with R³ or both R³ and R⁴; and iii) a ring system selected from 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes one or two O as ring members and optionally includes one or two ring members independently selected from C(=O) and S(O)₂, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic heterocyclic ring system optionally substituted with R^3 or both R^3 and R^4 ;

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A is O, S, N, NR⁵ or CR¹⁴;

G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A;

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W is O, S, NH, N(C₁-C₆ alkyl) or NO(C₁-C₆ alkyl);

X is H, OR¹, S(O)_mR¹, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₃-C₆ cycloalkyl, cyano, NH₂, NHR¹, N(C₁-C₆ alkyl)R¹, NH(C₁-C₆ alkoxy) or N(C₁-C₆ alkoxy)R¹;

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R¹ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl;

R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, hydroxy, C₁-C₂ alkoxy or acetyloxy;

R³ and R⁴ are each independently halogen; cyano; nitro; hydroxy; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyloxy; C₂-C₆ alkynyloxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; formyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxycarbonyl; NH₂C(O); (C₁-C₄ alkyl)NHC(O); (C₁-C₄ alkyl)₂NC(O); Si(R²⁵)₃; Ge(R²⁵)₃; (R²⁵)₃Si-C≡C-; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R⁸ and optionally substituted with one or more R¹⁰; or

when E is 1,2-phenylene and R³ and R⁴ are attached to adjacent atoms, R³ and R⁴ can be taken together as C₃-C₅ alkylene, C₃-C₅ haloalkylene, C₃-C₅ alkenylene or C₃-C₅ haloalkenylene each optionally substituted with 1-2 C₁-C₃ alkyl;

20 R⁵ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl;

Y is -O-, -S(O)_n-, -NR¹⁵-, -C(=O)-, -CH(OR¹⁵)-, -CHR⁶-, -CHR⁶CHR⁶-, -CR⁶=CR⁶-, -C=C-, -CHR¹⁵O-, -OCHR¹⁵-, -CHR¹⁵S(O)_n-, -S(O)_nCHR¹⁵-, -CHR¹⁵O-N=C(R⁷)-, -(R⁷)C=N-OCH(R¹⁵)-, -C(R⁷)=N-O-, -O-N=C(R⁷)-, -CHR¹⁵OC(=O)N(R¹⁵)-, -CHR¹⁵OC(=S)N(R¹⁵)-, -CHR¹⁵OC(=O)O-, -CHR¹⁵OC(=S)O-, -CHR¹⁵OC(=O)S-, -CHR¹⁵OC(=S)S-, -CHR¹⁵SC(=O)N(R¹⁵)-, -CHR¹⁵SC(=O)O-, -CHR¹⁵SC(=S)O-, -CHR¹⁵SC(=O)S-, -CHR¹⁵SC(=S)S-, -CHR¹⁵SC(=NR¹⁵)S-, -CHR¹⁵N(R¹⁵)C(=O)N(R¹⁵)-,

-CHR¹⁵O-N(R¹⁵)C(=O)N(R¹⁵)-, -CHR¹⁵O-N(R¹⁵)C(=S)N(R¹⁵)-,
-CHR¹⁵O-N=C(R⁷)NR¹⁵-, -CHR¹⁵O-N=C(R⁷)OCH₂-,
-CHR¹⁵O-N=C(R⁷)-N=N-, -CHR¹⁵O-N=C(R⁷)-C(=O)-,
-CHR¹⁵O-N=C(R⁷)-C(=N-A²-Z¹)-A¹-,

35 -CHR¹⁵O-N=C(R⁷)-C(R⁷)=N-A²-A³-, -CHR¹⁵O-N=C(-C(R⁷)=N-A²-Z¹)-, -CHR¹⁵O-N=C(R⁷)-CH₂O-, -CHR¹⁵O-N=C(R⁷)-CH₂S-, -O-CH₂CH₂O-N=C(R⁷)-, -CHR¹⁵O-C(R¹⁵)=C(R⁷)-, -CHR¹⁵O-C(R⁷)=N-, -CHR¹⁵S-C(R⁷)=N-, -C(R⁷)=N-NR¹⁵-, -CH=N-N=C(R⁷)-,

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-CHR¹⁵N(R¹⁵)-N=C(R⁷)-, -CHR¹⁵N(COCH₃)-N=C(R⁷)-, -OC(=S)NR¹⁵C(=O)-, -CHR⁶-C(=W¹)-A¹-, -CHR⁶CHR⁶-C(=W¹)-A¹-, -CR⁶=CR⁶-C(=W¹)-A¹-, -C=C-C(=W¹)-A¹-, -N=CR⁶-C(=W¹)-A¹- or a direct bond; and the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to E and the moiety on the right side of the linkage is bonded to Z;

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 Z^1 is H or $-A^3$ -Z;

W1 is O or S;

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A¹ is O, S, NR¹⁵ or a direct bond;

10 A² is O, NR¹⁵ or a direct bond;

 A^3 is -C(=O)-, -S(O)₂- or a direct bond;

each R⁶ is independently H, 1-2 CH₃, C₂-C₃ alkyl, C₁-C₃ alkoxy,

C₃-C₆ cycloalkyl, formylamino, C₂-C₄ alkylcarbonylamino,

C2-C4 alkoxycarbonylamino, NH2C(O)NH, (C1-C3 alkyl)NHC(O)NH,

(C₁-C₃ alkyl)₂NC(O)NH, N(C₁-C₃ alkyl)₂, piperidinyl, morpholinyl,

1-2 halogen, cyano or nitro;

each R⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy,

C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfinyl,

C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylthio, C₁-C₆ haloalkylsulfinyl,

C₁-C₆ haloalkylsulfonyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl,

C2-C6 haloalkynyl, C3-C6 cycloalkyl, C2-C4 alkylcarbonyl,

C2-C4 alkoxycarbonyl, halogen, cyano, nitro, hydroxy, amino,

 $NH(C_1-C_6 \text{ alkyl}), N(C_1-C_6 \text{ alkyl})_2 \text{ or morpholinyl};$

each Z is independently selected from:

i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl and C₂-C₁₀ alkynyl each substituted with R⁹ and optionally substituted with one or more R¹⁰;

ii) C₃-C₈ cycloalkyl, C₃-C₈ cycloalkenyl and phenyl each substituted with R⁹ and optionally substituted with one or more R¹⁰;

iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic and fused tricyclic nonaromatic heterocyclic ring systems and 5 to 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each nonaromatic or aromatic heterocyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰;

iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic

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and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing one or two nonaromatic rings that each include one or two Q as ring members and one or two ring members independently selected from C(=O) and S(O)₂, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰; and

- v) adamantyl substituted with R⁹ and optionally substituted with one or more R¹⁰;
- each Q is independently selected from the group -CHR¹³-, -NR¹³-, -O- and -S(O)_D-;

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- R⁸ is H, 1-2 halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy,

 C₁-C₆ haloalkoxy, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl,

 C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl,

 C₁-C₆ alkylsulfonyl, C₃-C₆ cycloalkyl, C₃-C₆ alkenyloxy,

 CO₂(C₁-C₆ alkyl), NH(C₁-C₆ alkyl), N(C₁-C₆ alkyl)₂, cyano, nitro,

 SiR¹⁹R²⁰R²¹ or GeR¹⁹R²⁰R²¹:
- R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy;

 C₁-C₆ haloalkoxy; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl;

 C₁-C₆ alkylthio; C₁-C₆ haloalkylthio; C₁-C₆ alkylsulfinyl;

 C₁-C₆ alkylsulfonyl; C₃-C₆ cycloalkyl; C₃-C₆ alkenyloxy;

 CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; -C(R¹⁸)=NOR¹⁷;

 cyano; nitro; SF₅; SiR²²R²³R²⁴; or GeR²²R²³R²⁴; or R⁹ is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl,

 pyrimidinyl, or pyrimidinyloxy each optionally substituted with one of R¹¹,

 R¹², or both R¹¹ and R¹²;
 - each R^{10} is independently halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, nitro or cyano; or
 - when R⁹ and an R¹⁰ are attached to adjacent atoms on Z, R⁹ and said adjacently attached R¹⁰ can be taken together as -OCH₂O- or -OCH₂CH₂O-; each CH₂ group of said taken together R⁹ and R¹⁰ optionally substituted with 1-2 halogen; or
- when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is

 -CHR¹⁵O-N=C(R⁷)-, -O-N=C(R⁷)-, -O-CH₂CH₂O-N=C(R⁷)-,

 -CHR¹⁵O-C(R¹⁵)=C(R⁷)-, -CH=N-N=C(R⁷)-, -CHR¹⁵N(R¹⁵)-N=C(R⁷)- or

 -CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as -(CH₂)_r-J- such that J is attached to Z;

	J is -CH ₂ -, -CH ₂ CH ₂ -, -OCH ₂ -, -CH ₂ O-, -SCH ₂ -, -CH ₂ S-, -N(R ¹⁶)CH ₂ - or
	-CH ₂ N(R ¹⁶)-; each CH ₂ group of said J optionally substituted with 1 to 2
	CH ₃ ;
	R ¹¹ and R ¹² are each independently 1-2 halogen; C ₁ -C ₄ alkyl; C ₁ -C ₄ haloalkyl;
5	C ₂ -C ₆ alkenyl; C ₂ -C ₆ haloalkenyl; C ₂ -C ₆ alkynyl; C ₂ -C ₆ haloalkynyl;
	C ₂ -C ₆ alkoxyalkyl; C ₂ -C ₆ alkylthioalkyl; C ₃ -C ₆ alkoxyalkynyl;
	C ₇ -C ₁₀ tetrahydropyranyloxyalkynyl; benzyloxymethyl; C ₁ -C ₄ alkoxy;
	C ₁ -C ₄ haloalkoxy; C ₃ -C ₆ alkenyloxy; C ₃ -C ₆ haloalkenyloxy;
	C ₃ -C ₆ alkynyloxy; C ₃ -C ₆ haloalkynyloxy; C ₂ -C ₆ alkoxyalkoxy;
10	C ₅ -C ₉ trialkylsilylalkoxyalkoxy; C ₂ -C ₆ alkylthioalkoxy; C ₁ -C ₄ alkylthio;
	C ₁ -C ₄ haloalkylthio; C ₁ -C ₄ alkylsulfinyl; C ₁ -C ₄ haloalkylsulfinyl;
	C ₁ -C ₄ alkylsulfonyl; C ₁ -C ₄ haloalkylsulfonyl; C ₃ -C ₆ alkenylthio;
	C ₃ -C ₆ haloalkenylthio; C ₂ -C ₆ alkylthioalkylthio; nitro; cyano; thiocyanato;
	hydroxy; $N(R^{26})_2$; SF_5 ; $Si(R^{25})_3$; $Ge(R^{25})_3$; $(R^{25})_3Si-C=C-$; $OSi(R^{25})_3$;
15	$OGe(R^{25})_3$; $C(=O)R^{26}$; $C(=S)R^{26}$; $C(=O)OR^{26}$; $C(=S)OR^{26}$; $C(=O)SR^{26}$;
	$C(=S)SR^{26}$; $C(=O)N(R^{26})_2$; $C(=S)N(R^{26})_2$; $OC(=O)R^{26}$; $OC(=S)R^{26}$;
	$SC(=O)R^{26}$; $SC(=S)R^{26}$; $N(R^{26})C(=O)R^{26}$; $N(R^{26})C(=S)R^{26}$;
	$OC(=O)OR^{27}$; $OC(=O)SR^{27}$; $OC(=O)N(R^{26})_2$; $SC(=O)OR^{27}$; $SC(=O)SR^{27}$;
	$S(O)_2OR^{26}$; $S(O)_2N(R^{26})_2$; $OS(O)_2R^{27}$; $N(R^{26})S(O)_2R^{27}$; or phenyl,
20	phenoxy, benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or
	pyridinylethynyl, each optionally substituted with halogen, C ₁ -C ₄ alkyl,
	C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano;
	each R ¹³ is independently H; C ₁ -C ₆ alkyl; C ₁ -C ₆ haloalkyl; or phenyl optionally
	substituted with halogen, C ₁ -C ₄ alkyl, C ₁ -C ₄ haloalkyl, C ₁ -C ₄ alkoxy,
25	C ₁ -C ₄ haloalkoxy, nitro or cyano;
	R^{14} is H, halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl,
	C ₂ -C ₆ haloalkenyl, C ₂ -C ₆ alkynyl, C ₂ -C ₆ haloalkynyl or C ₃ -C ₆ cycloalkyl;
	each R ¹⁵ is independently H; C ₁ -C ₃ alkyl; C ₃ -C ₆ cycloalkyl; or phenyl or benzyl,
	each optionally substituted on the phenyl ring with halogen, C ₁ -C ₄ alkyl,
30	C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano; or
	when Y is -CHR ¹⁵ N(R ¹⁵)C(=O)N(R ¹⁵)-, the two R ¹⁵ attached to nitrogen atoms
	on said group can be taken together as -(CH ₂) _s -; or
	when Y is -CHR ¹⁵ O-N=C(R ⁷)NR ¹⁵ -, R ⁷ and the adjacently attached R ¹⁵ can be
2.5	taken together as -CH ₂ -(CH ₂) _s -, -O-(CH ₂) _s -, -S-(CH ₂) _s - or
35	-N(C ₁ -C ₃ alkyl)-(CH ₂) _s -; with the directionality of said linkage defined
	such that the moiety depicted on the left side of the linkage is bonded to the
	carbon and the moiety on the right side of the linkage is bonded to the
	nitrogen;

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R¹⁶, R¹⁷ and R¹⁸ are each independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

 $\rm R^{19},\,R^{20},\,R^{21},\,R^{22},\,R^{23}$ and $\rm R^{24}$ are each independently $\rm C_1\text{-}C_6$ alkyl,

C₂-C₆ alkenyl, C₁-C₄ alkoxy or phenyl;

each R^{25} is independently C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl, C_1 - C_4 alkoxy or phenyl;

each R²⁶ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

each R²⁷ is independently C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

m, n and p are each independently 0, 1 or 2;

r is 0 or 1; and

20 s is 2 or 3; and

(2) at least one compound selected from (a) compounds of Formula II, N-oxides, and agriculturally suitable salts thereof.

wherein

25 E¹ is

the directionally of the E¹ linkage is defined such that the moiety depicted on the left side of the linkage is bonded to carbon and the moiety on the right side

is bonded to nitrogen; and

30 R²⁸ is H or phenoxy;

- and (b) compounds that control fungal disease by inhibiting the sterol biosynthesis pathway; and optionally
- (3) at least one of a surfactant, a solid diluent or a liquid diluent; wherein component (1) and component (2) are present in a fungicidally effective amount and the mole ratio of component (1) to component (2) is from about 15:1 to 1:15.
 - 2. The fungicidal composition of Claim 1 comprising a fungicidally effective amount of (1) at least one compound selected from the compounds of Formula I, N-oxides, and agriculturally suitable salts thereof, wherein
- 10 E is selected from the group 1,2-phenylene; 1,5-, 1,6-, 1,7-, 1,8-, 2,6-, 2,7-, 1,2-, and 2,3-naphthalenediyl; 1H-pyrrole-1,2-, 2,3- and 3,4-diyl; 2,3- and 3,4-furandiyl; 2,3- and 3,4-thiophenediyl; 1H-pyrazole-1,5-, 3,4- and 4,5-diyl; 1*H*-imidazole-1,2-, 4,5- and 1,5-diyl; 3,4- and 4,5-isoxazolediyl; 4.5-oxazolediyl: 3.4- and 4.5-isothiazolediyl: 4.5-thiazolediyl: 1*H*-1,2,3-triazole-1,5- and 4,5-diyl; 2*H*-1,2,3-triazole-4,5-diyl; 15 1*H*-1,2,4-triazole-1,5-diyl; 4*H*-1,2,4-triazole-3,4-diyl; 1,2,3-oxadiazole-4,5-diyl; 1,2,5-oxadiazole-3,4-diyl; 1.2.3-thiadiazole-4.5-diyl; 1.2.5-thiadiazole-3.4-diyl; 1H-tetrazole-1.5-diyl; 2,3- and 3,4-pyridinediyl; 3,4- and 4,5-pyridazinediyl; 4,5-pyrimidinediyl; 2,3-pyrazinediyl; 1,2,3-triazine-4,5-diyl; 1,2,4-triazine-5,6-diyl; 20 1H-indole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 1,2-, 2,3-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 2,3-, 4,5-, 5,6- and 6,7-benzofurandiyl; benzo[b]thiophene-2,4-, 2,5-, 2,6-, 2.7-, 3.4-, 3.5-, 3.6-, 3.7-, 2.3-, 4.5-, 5.6- and 6.7-diyl; 1H-indazole-1,4-, 1,5-, 1,6-, 1,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6.7-divl; 25 1H-benzimidazole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-diyl; 1,2-benzisoxazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-benzoxazolediyl; 1,2-benzisothiazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 30 6,7-benzothiazolediyl; 2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 2,3-, 3,4-, 5,6-, 6,7- and 7,8-quinolinediyl; 1,5-, 1,6-, 1,7-, 1,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and 7,8-isoquinolinediyl; 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and 7,8-cinnolinediyl; 1,5-, 1,6-, 1,7-, 1,8-, 5,6-, 6,7- and 35 7,8-phthalazinediyl; 2,5-, 2,6-, 2,7-, 2,8-, 4,5-, 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and 7,8-quinazolinediyl; 2,5-, 2,6-, 2,7-, 2,8-, 2,3-, 5,6-, 6,7- and 7,8-quinoxalinediyl; 1,8,-naphthyridine-2,5-, 2,6-, 2,7-, 3,5-, 3,6-, 4,5-, 2,3and 3,4-diyl; 2,6-, 2,7-, 4,6-, 4,7-, 6,7-pteridinediyl;

pyrazolo[5,1-b]thiazole-2,6-, 2,7-, 3,6-, 3,7-, 2,3- and 6,7-divl: thiazolo[2,3-c]-1,2,4-triazole-2,5-, 2,6-, 5,6-divl: 2-oxo-1,3-benzodioxole-4,5- and 5,6-diyl; 1,3-dioxo-1H-isoindole-2,4-, 2,5-, 4,5- and 5,6-diyl; 2-oxo-2*H*-1-benzopyran-3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 5 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and 7,8-diyl; [1,2,4]triazolo[1,5-a]pyridine-2,5-, 2,6-, 2,7-, 2,8-, 5,6-, 6,7- and 7,8-diyl; 3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazine-3,5-, 3,6-, 3,7-, 3,8-, 5,6-, 6,7and 7,8-diyl; 2,3-dihydro-2-oxo-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-benzofurandiyl; thieno[3,2-d]thiazole-2,5-, 2,6-, and 5,6-divl: 10 5,6,7,8-tetrahydro-2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 2,3- and 3,4-quinolinediyl; 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazole-2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6and 6,7-diyl; 1,3-benzodioxole-2,4-, 2,5-, 4,5- and 5,6-diyl; 2,3-dihydro-2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 15 6,7-benzofurandiyl; 2,3-dihydro-1,4-benzodioxin-2,5-, 2,6-, 2,7-, 2,8-, 5,6and 6,7-diyl; and 5,6,7,8-tetrahydro-4H-cyclohepta[b]thiophene-2,4-, 2,5-, 2,6-, 2,7-, 2,8-, 3,4-, 3,5-, 3,6-, 3,7-, 3,8-, and 2,3-divl; each aromatic ring system optionally substituted with one of R³, R⁴, or both R³ and R⁴; W is O: 20 R^1 is C_1 - C_3 alkyl or C_1 - C_3 haloalkyl; R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl or C₃-C₆ cycloalkyl; R³ and R⁴ are each independently halogen, cyano, nitro, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfonyl, C2-C6 alkylcarbonyl, C2-C6 alkoxycarbonyl, 25 (C₁-C₄ alkyl)NHC(O), (C₁-C₄ alkyl)₂NC(O), benzoyl or phenylsulfonyl; Y is -O-, -S(O)_n-, -NR¹⁵-, -C(=O)-, -CH(OR¹⁵)-, -CH₂-, -CH₂CH₂-, -CH=CH-, $-C \equiv C_{-}, -CH_{2}O_{-}, -OCH_{2^{-}}, -CH_{2}S(O)_{n^{-}}, -S(O)_{n}CH_{2^{-}}, -CH_{2}O-N=C(R^{7})_{-}$ - (R^7) C=N-OCH (R^{15}) -, - $C(R^7)$ =N-O- or a direct bond; R⁷ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, C₂-C₆ 30 alkenyl, C2-C6 alkynyl, C3-C6 cycloalkyl, halogen or cyano; or when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is -CH₂O-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as -(CH₂)_r-J- such that J is attached to Z; Z is selected from the group C₁-C₁₀ alkyl; C₃-C₈ cycloalkyl; phenyl; 35 naphthalenyl; anthracenyl; phenanthrenyl; 1H-pyrrolyl; furanyl; thienyl; 1*H*-pyrazolyl; 1*H*-imidazolyl; isoxazolyl; oxazolyl; isothiazolyl; thiazolyl; 1*H*-1,2,3-triazolyl; 2*H*-1,2,3-triazolyl; 1*H*-1,2,4-triazolyl; 4H-1,2,4-triazolyl; 1,2,3-oxadiazolyl; 1,2,4-oxadiazolyl; 1,2,5-oxadiazolyl;

1,3,4-oxadiazolyl; 1,2,3-thiadiazolyl; 1,2,4-thiadiazolyl; 1,2,5-thiadiazolyl; 1,3,4-thiadiazolyl; 1H-tetrazolyl; 2H-tetrazolyl; pyridinyl; pyridazinyl; pyrimidinyl; pyrazinyl; 1,3,5-triazinyl; 1,2,4-triazinyl; 1,2,4,5-tetrazinyl; 1*H*-indolyl; benzofuranyl; benzo[*b*]thiophenyl; 1*H*-indazolyl; 5 1H-benzimidazolyl; benzoxazolyl; benzothiazolyl; quinolinyl; isoquinolinyl; cinnolinyl; phthalazinyl; quinazolinyl; quinoxalinyl; 1,8-naphthyridinyl; pteridinyl; 2,3-dihydro-1*H*-indenyl; 1,2,3,4-tetrahydronaphthalenyl; 6,7,8,9-tetrahydro-5*H*-benzocycloheptenyl; 5,6,7,8,9,10-hexahydrobenzocyclooctenyl; 2,3-dihydro-3-oxobenzofuranyl; 1,3-dihydro-1-oxoisobenzofuranyl; 2,3-dihydro-2-oxobenzofuranyl; 10 3,4-dihydro-4-oxo-2*H*-1-benzopyranyl; 3,4-dihydro-1-oxo-1*H*-2-benzopyranyl; 3,4-dihydro-3-oxo-1*H*-2-benzopyranyl; 3,4-dihydro-2-oxo-2*H*-1-benzopyranyl; 4-oxo-4*H*-1-benzopyranyl; 15 2-oxo-2*H*-1-benzopyranyl; 2,3,4,5-tetrahydro-5-oxo-1-benzoxepinyl; 2,3,4,5-tetrahydro-2-oxo-1-benzoxepinyl; 2,3-dihydro-1,3-dioxo-1*H*-isoindolyl: 1,2,3,4-tetrahydro-1,3-dioxoisoguinolinyl; 3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazinyl; 2-oxo-1,3-benzodioxyl; 20 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazolyl; 9H-fluorenyl; azulenyl; and thiazolo[2,3-c]-1,2,4-triazolyl; each group substituted with R^9 and optionally substituted with one or more R¹⁰: R¹⁵ is H, C₁-C₃ alkyl or C₃-C₆ cycloalkyl; and (2) at least one compound selected from the compounds of (a) Formula II. 25 N-oxides, and agriculturally suitable salts thereof, and (b) bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenarimol, fenbuconazole, fenpropidin, fenpropimorph, fluquinconazole, flusilazole, flutriafol, hexaconazole, ipconazole, metconazole, penconazole, prochloraz, propiconazole, tebuconazole, 30 tetraconazole, triadimenol, tridemorph, triticonazole and uniconazole.

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- 3. The fungicidal composition of Claim 2 comprising a fungicidally effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and (2) of at least one compound selected from the group consisting of (a) 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione and 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4*H*-imidazol-4-one and (b) epoxiconazole, fenpropimorph, flusilazole, propiconazole and tebuconazole.
- 4. The fungicidal composition of Claim 2 comprising a fungicidally effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and (2) 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione.
- 5. The fungicidal composition of Claim 2 comprising a fungicidally effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and (2) flusilazole.
- 6. The fungicidal composition of Claim 2 comprising a fungicidally effective amount of (1) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and (2) both 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione and flusilazole.
- 7. A method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of a composition of Claim 1.
- 8. A method of controlling *Erysiphe graminis* comprising applying to the plant or portion thereof, or to the plant seed or seedling (1) at least one compound selected from the compounds of Formula I, N-oxides, and agriculturally suitable salts thereof,

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wherein

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E is selected from:

i) 1,2-phenylene optionally substituted with R³ or both R³ and R⁴; ii) naphthalenediyl, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalenediyl optionally substituted with R³ or both R³ and R⁴; and iii) a ring system selected from 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes one or two Q as ring members and optionally includes one or two ring members independently selected from C(=O) and S(O)₂, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic heterocyclic ring system optionally substituted with R³ or both R³ and R⁴:

A is O, S, N, NR5 or CR14;

G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A;

W is O, S, NH, $N(C_1-C_6 \text{ alkyl})$ or $NO(C_1-C_6 \text{ alkyl})$;

- X is H, OR¹, S(O)_mR¹, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₃-C₆ cycloalkyl, cyano, NH₂, NHR¹, N(C₁-C₆ alkyl)R¹, NH(C₁-C₆ alkoxy) or N(C₁-C₆ alkoxy)R¹;
- R¹ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl;
- R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, hydroxy, C₁-C₂ alkoxy or acetyloxy;
- R³ and R⁴ are each independently halogen; cyano; nitro; hydroxy; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl;

 C₂-C₆ haloalkynyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyloxy;

 C₂-C₆ alkynyloxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl;

 C₁-C₆ alkylsulfonyl; formyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxycarbonyl;

 NH₂C(O); (C₁-C₄ alkyl)NHC(O); (C₁-C₄ alkyl)₂NC(O); Si(R²⁵)₃;

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 $Ge(R^{25})_3$; $(R^{25})_3Si-C=C-$; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R^8 and optionally substituted with one or more R^{10} ; or

when E is 1,2-phenylene and R³ and R⁴ are attached to adjacent atoms, R³ and R⁴ can be taken together as C₃-C₅ alkylene, C₃-C₅ haloalkylene, C₃-C₅ alkenylene or C₃-C₅ haloalkenylene each optionally substituted with 1-2 C₁-C₃ alkyl;

R⁵ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl;

Y is -O-, -S(O)_n-, -NR¹⁵-, -C(=O)-, -CH(OR¹⁵)-, -CHR⁶-, -CHR⁶CHR⁶-, -CR⁶=CR⁶-, -C=C-, -CHR¹⁵O-, -OCHR¹⁵-, -CHR¹⁵S(O)_n-, -S(O)_nCHR¹⁵-, -CHR¹⁵O-N=C(R⁷)-, -(R⁷)C=N-OCH(R¹⁵)-, -C(R⁷)=N-O-, -O-N=C(R⁷)-, -CHR¹⁵OC(=O)N(R¹⁵)-, -CHR¹⁵OC(=O)O-, -CHR¹⁵OC(=S)O-, -CHR¹⁵OC(=O)S-, -CHR¹⁵OC(=S)S-,

-CHR¹⁵SC(=O)N(R¹⁵)-, -CHR¹⁵SC(=S)N(R¹⁵)-, -CHR¹⁵SC(=O)O-,

-CHR¹⁵SC(=S)O-, -CHR¹⁵SC(=O)S-, -CHR¹⁵SC(=S)S-,

-CHR 15 SC(=NR 15)S-, -CHR 15 N(R 15)C(=O)N(R 15)-,

 $-CHR^{15}O-N(R^{15})C(=O)N(R^{15})-, -CHR^{15}O-N(R^{15})C(=S)N(R^{15})-, -CHR^{15}O-N(R^{15})-, -CHR^{15}O-N(R^{$

-CHR¹⁵O-N=C(\mathbb{R}^7)NR¹⁵-, -CHR¹⁵O-N=C(\mathbb{R}^7)OCH₂-,

-CHR¹⁵O-N=C(R⁷)-N=N-, -CHR¹⁵O-N=C(R⁷)-C(=O)-,

-CHR 15 O-N=C(R 7)-C(=N-A 2 -Z 1)-A 1 -,

-CHR¹⁵O-N=C(R⁷)-C(R⁷)=N-A²-A³-, -CHR¹⁵O-N=C(-C(R⁷)=N-A²-Z¹)-,

-CHR¹⁵O-N=C(R⁷)-CH₂O-, -CHR¹⁵O-N=C(R⁷)-CH₂S-,

-O- $CH_2CH_2O-N=C(R^7)-$, - $CHR^{15}O-C(R^{15})=C(R^7)-$, - $CHR^{15}O-C(R^7)=N-$,

-CHR¹⁵S-C(R⁷)=N-, -C(R⁷)=N-NR¹⁵-, -CH=N-N=C(R⁷)-,

-CHR¹⁵N(R¹⁵)-N=C(R⁷)-, -CHR¹⁵N(COCH₃)-N=C(R⁷)-,

 $-OC(=S)NR^{15}C(=O)-, -CHR^6-C(=W^1)-A^1-, -CHR^6CHR^6-C(=W^1)-A^1-, -CHR^6CHR^6-C(=W^1)-A^1-, -CHR^6CHR^6-C(=W^1)-A^1-, -CHR^6-C(=W^1)-A^1-, -CHR^6-C(=W^$

-CR6=CR6-C(=W1)-A1-, -C=C-C(=W1)-A1-, -N=CR6-C(=W1)-A1- or a

direct bond; and the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to E and the moiety on the right side of the linkage is bonded to Z;

 Z^1 is H or -A³-Z;

W1 is O or S;

35 A¹ is O, S, NR¹⁵ or a direct bond;

A² is O, NR¹⁵ or a direct bond;

 A^3 is -C(=O)-, -S(O)₂- or a direct bond;

each R⁶ is independently H, 1-2 CH₃, C₂-C₃ alkyl, C₁-C₃ alkoxy, C₃-C₆ cycloalkyl, formylamino, C₂-C₄ alkylcarbonylamino, C2-C4 alkoxycarbonylamino, NH2C(O)NH, (C1-C3 alkyl)NHC(O)NH, (C₁-C₃ alkyl)₂NC(O)NH, N(C₁-C₃ alkyl)₂, piperidinyl, morpholinyl, 5 1-2 halogen, cyano or nitro; each R⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylthio, C₁-C₆ haloalkylsulfinyl, C₁-C₆ haloalkylsulfonyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, 10 C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, halogen, cyano, nitro, hydroxy, amino, $NH(C_1-C_6 \text{ alkyl})$, $N(C_1-C_6 \text{ alkyl})$ 2 or morpholinyl; each Z is independently selected from: i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl and C₂-C₁₀ alkynyl each substituted with 15 R^9 and optionally substituted with one or more R^{10} ; ii) C3-C8 cycloalkyl, C3-C8 cycloalkenyl and phenyl each substituted with R^9 and optionally substituted with one or more R^{10} : iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic and fused tricyclic nonaromatic heterocyclic ring systems and 5 to 20 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each 25 nonaromatic or aromatic heterocyclic ring system substituted with R9 and optionally substituted with one or more R¹⁰; iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing 30 one or two nonaromatic rings that each include one or two Q as ring members and one or two ring members independently selected from C(=0) and S(O)₂, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰; and 35 v) adamantyl substituted with R⁹ and optionally substituted with one or each Q is independently selected from the group -CHR¹³-, -NR¹³-, -O- and

 $-S(O)_{p}$ -;

R8 is H, 1-2 halogen, C1-C6 alkyl, C1-C6 haloalkyl, C1-C6 alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₃-C₆ cycloalkyl, C₃-C₆ alkenyloxy, 5 CO₂(C₁-C₆ alkyl), NH(C₁-C₆ alkyl), N(C₁-C₆ alkyl)₂, cyano, nitro, SiR 19R20R21 or GeR 19R20R21: R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₁-C₆ alkylthio; C₁-C₆ haloalkylthio; C₁-C₆ alkylsulfinyl; 10 C₁-C₆ alkylsulfonyl; C₃-C₆ cycloalkyl; C₃-C₆ alkenyloxy; $CO_2(C_1-C_6 \text{ alkyl}); NH(C_1-C_6 \text{ alkyl}); N(C_1-C_6 \text{ alkyl})_2; -C(R^{18})=NOR^{17};$ cyano; nitro; SF₅; SiR²²R²³R²⁴; or GeR²²R²³R²⁴; or R⁹ is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl, or pyrimidinyloxy each optionally substituted with one of R¹¹, R12, or both R11 and R12; 15 each R¹⁰ is independently halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, nitro or cyano; or when R⁹ and an R¹⁰ are attached to adjacent atoms on Z, R⁹ and said adjacently attached R¹⁰ can be taken together as -OCH₂O- or -OCH₂CH₂O-; each CH₂ group of said taken together R⁹ and R¹⁰ optionally substituted with 1-2 20 halogen; or when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is -CHR¹⁵O-N=C(R⁷)-, -O-N=C(R⁷)-, -O-CH₂CH₂O-N=C(R⁷)-, -CHR¹⁵O-C(R^{15})=C(R^7)-, -CH=N-N=C(R^7)-, -CHR¹⁵N(R^{15})-N=C(R^7)- or -CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be 25 taken together as -(CH₂)_r-J- such that J is attached to Z; J is -CH₂-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -N(R¹⁶)CH₂- or -CH₂N(R¹⁶)-; each CH₂ group of said J optionally substituted with 1 to 2 CH₃; 30 R¹¹ and R¹² are each independently 1-2 halogen; C₁-C₄ alkyl; C₁-C₄ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₂-C₆ alkoxyalkyl; C₂-C₆ alkylthioalkyl; C₃-C₆ alkoxyalkynyl; C_7 - C_{10} tetrahydropyranyloxyalkynyl; benzyloxymethyl; C_1 - C_4 alkoxy; C₁-C₄ haloalkoxy; C₃-C₆ alkenyloxy; C₃-C₆ haloalkenyloxy; 35 C₃-C₆ alkynyloxy; C₃-C₆ haloalkynyloxy; C₂-C₆ alkoxyalkoxy; C₅-C₉ trialkylsilylalkoxyalkoxy; C₂-C₆ alkylthioalkoxy; C₁-C₄ alkylthio; C_1 - C_4 haloalkylthio; C_1 - C_4 alkylsulfinyl; C_1 - C_4 haloalkylsulfinyl;

C₁-C₄ alkylsulfonyl; C₁-C₄ haloalkylsulfonyl; C₂-C₆ alkenylthio;

C₃-C₆ haloalkenylthio; C₂-C₆ alkylthioalkylthio; nitro; cyano; thiocyanato; hydroxy; $N(R^{26})_2$; SF_5 ; $Si(R^{25})_3$; $Ge(R^{25})_3$; $(R^{25})_3Si-C=C-$; $OSi(R^{25})_3$; $OGe(R^{25})_3$; $C(=O)R^{26}$; $C(=S)R^{26}$; $C(=O)OR^{26}$; $C(=S)OR^{26}$; $C(=O)SR^{26}$; $C(=S)SR^{26}$; $C(=O)N(R^{26})_2$; $C(=S)N(R^{26})_2$; $OC(=O)R^{26}$; $OC(=S)R^{26}$; $SC(=O)R^{26}$; $SC(=S)R^{26}$; $N(R^{26})C(=O)R^{26}$; $N(R^{26})C(=S)R^{26}$; 5 $OC(=O)OR^{27}$; $OC(=O)SR^{27}$; $OC(=O)N(R^{26})$; $SC(=O)OR^{27}$; $SC(=O)SR^{27}$; $S(O)_2OR^{26}$; $S(O)_2N(R^{26})_2$; $OS(O)_2R^{27}$; $N(R^{26})S(O)_2R^{27}$; or phenyl, phenoxy, benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or pyridinylethynyl, each optionally substituted with halogen, C₁-C₄ alkyl, 10 C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; each R¹³ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano; R¹⁴ is H, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, 15 C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl or C₃-C₆ cycloalkyl; each R¹⁵ is independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; or when Y is -CHR¹⁵N(R¹⁵)C(=O)N(R¹⁵)-, the two R¹⁵ attached to nitrogen atoms 20 on said group can be taken together as -(CH₂)_s-; or when Y is -CHR¹⁵O-N=C(R⁷)NR¹⁵-, R⁷ and the adjacently attached R¹⁵ can be taken together as -CH₂-(CH₂)_S-, -O-(CH₂)_S-, -S-(CH₂)_S- or -N(C₁-C₃ alkyl)-(CH₂)_s-; with the directionality of said linkage defined such that the moiety depicted on the left side of the linkage is bonded to the 25 carbon and the moiety on the right side of the linkage is bonded to the nitrogen; R¹⁶, R¹⁷ and R¹⁸ are each independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl optionally substituted with halogen, C1-C4 alkyl, C1-C4 haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; R¹⁹, R²⁰, R²¹, R²², R²³ and R²⁴ are each independently C₁-C₆ alkyl, 30 C₂-C₆ alkenyl, C₁-C₄ alkoxy or phenyl; each R²⁵ is independently C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₄ alkenyl, C₁-C₄ alkoxy or phenyl; each R²⁶ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; 35 C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with

halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy,

nitro or cyano;

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each R²⁷ is independently C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

m, n and p are each independently 0, 1 or 2;

r is 0 or 1; and

s is 2 or 3; and

(2) at least one compound selected from compounds of Formula II, N-oxides, and agriculturally suitable salts thereof,

wherein

E¹ is

the directionally of the E¹ linkage is defined such that the moiety depicted on the left side of the linkage is bonded to carbon and the moiety on the right side is bonded to nitrogen; and

R²⁸ is H or phenoxy;

wherein component (1) and component (2) are added in amounts sufficient to provide a fungicidal effectiveness greater than the sum of the fungicidal effectivenesses of the amounts of said components taken independently.

- 9. A method of Claim 8 wherein component (1) is 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,4-triazol-3-one and component (2) is selected from the group consisting of 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl-amino)-2,4-oxazolidinedione and 3,5-dihydro 5-methyl-2-(methylthio)-5-phenyl-3-(phenylamino)-4H-imidazol-4-one; and wherein the mole ratio of component (1) to component (2) is from 15:1 to 1:15.
- 10. A method for the preventative control of *Septoria nodorum* comprising applying to the plant or portion thereof, or to the plant seed or seedling (1) at least one

compound selected from the compounds of Formula I, N-oxides, and agriculturally suitable salts thereof,

5 wherein

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E is selected from:

i) 1,2-phenylene optionally substituted with R³ or both R³ and R⁴; ii) naphthalenediyl, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalenediyl optionally substituted with R³ or both R³ and R⁴; and iii) a ring system selected from 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes one or two Q as ring members and optionally includes one or two ring members independently selected from C(=O) and S(O)₂, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic heterocyclic ring system optionally substituted with R³ or both R³ and R⁴;

A is O, S, N, NR⁵ or CR¹⁴;

G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A;

W is O, S, NH, $N(C_1-C_6 \text{ alkyl})$ or $NO(C_1-C_6 \text{ alkyl})$;

X is H, OR^1 , $S(O)_mR^1$, halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_3 - C_6 cycloalkyl, cyano, NH_2 , NHR^1 , $N(C_1$ - C_6 alkyl) R^1 , $NH(C_1$ - C_6 alkoxy) or $N(C_1$ - C_6 alkoxy) R^1 ;

R¹ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl; R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, 5 C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, hydroxy, C₁-C₂ alkoxy or acetyloxy; R³ and R⁴ are each independently halogen; cyano; nitro; hydroxy; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyloxy; 10 C₂-C₆ alkynyloxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; formyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxycarbonyl; $NH_2C(O)$; $(C_1-C_4 \text{ alkyl})NHC(O)$; $(C_1-C_4 \text{ alkyl})_2NC(O)$; $Si(R^{25})_3$; $Ge(R^{25})_3$; $(R^{25})_3Si-C=C-$; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R⁸ and optionally substituted with one 15 or more R¹⁰; or when E is 1,2-phenylene and R³ and R⁴ are attached to adjacent atoms, R³ and R⁴ can be taken together as C₃-C₅ alkylene, C₃-C₅ haloalkylene, C₃-C₅ alkenylene or C₃-C₅ haloalkenylene each optionally substituted with $1-2 C_1-C_3$ alkyl; 20 R⁵ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl; Y is -O-, -S(O)_n-, -NR¹⁵-, -C(=O)-, -CH(OR¹⁵)-, -CHR⁶-, -CHR⁶-CHR⁶-, -CR6=CR6-, -C=C-, -CHR15O-, -OCHR15-, -CHR15S(O)n-, -S(O)nCHR15-, 25 $-CHR^{15}O-N=C(R^7)-$, $-(R^7)C=N-OCH(R^{15})-$, $-C(R^7)=N-O-$, $-O-N=C(R^7)-$, -CHR¹⁵OC(=O)N(R¹⁵)-, -CHR¹⁵OC(=S)N(R¹⁵)-, -CHR¹⁵OC(=O)O-, -CHR¹⁵OC(=S)O-, -CHR¹⁵OC(=O)S-, -CHR¹⁵OC(=S)S-, -CHR¹⁵SC(=O)N(R¹⁵)-, -CHR¹⁵SC(=S)N(R¹⁵)-, -CHR¹⁵SC(=O)O-, -CHR¹⁵SC(=S)O-, -CHR¹⁵SC(=O)S-, -CHR¹⁵SC(=S)S-, $-CHR^{15}SC(=NR^{15})S-$, $-CHR^{15}N(R^{15})C(=O)N(R^{15})-$, 30 $-CHR^{15}O-N(R^{15})C(=O)N(R^{15})-$, $-CHR^{15}O-N(R^{15})C(=S)N(R^{15})-$, -CHR¹⁵O-N=C(R⁷)NR¹⁵-, -CHR¹⁵O-N=C(R⁷)OCH₂-, $-CHR^{15}O-N=C(R^7)-N=N-, -CHR^{15}O-N=C(R^7)-C(=O)-,$ $-CHR^{15}O-N=C(R^7)-C(=N-A^2-Z^1)-A^1$ $-CHR^{15}O-N=C(R^7)-C(R^7)=N-A^2-A^3-$, $-CHR^{15}O-N=C(-C(R^7)=N-A^2-Z^1)-$ 35 -CHR¹⁵O-N=C(R⁷)-CH₂O-, -CHR¹⁵O-N=C(R⁷)-CH₂S-, $-O-CH_2CH_2O-N=C(R^7)-$, $-CHR^{15}O-C(R^{15})=C(R^7)-$, $-CHR^{15}O-C(R^7)=N-$,

 $-CHR^{15}S-C(R^7)=N-, -C(R^7)=N-NR^{15}-, -CH=N-N=C(R^7)-,$

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-CHR¹⁵N(R¹⁵)-N=C(R⁷)-, -CHR¹⁵N(COCH₃)-N=C(R⁷)-,
-OC(=S)NR¹⁵C(=O)-, -CHR⁶-C(=W¹)-A¹-, -CHR⁶CHR⁶-C(=W¹)-A¹-,
-CR⁶=CR⁶-C(=W¹)-A¹-, -C=C-C(=W¹)-A¹-, -N=CR⁶-C(=W¹)-A¹- or a
direct bond; and the directionality of the Y linkage is defined such that the
moiety depicted on the left side of the linkage is bonded to E and the moiety
on the right side of the linkage is bonded to Z;

 Z^1 is H or $-A^3$ -Z;

W¹ is O or S;

A¹ is O, S, NR¹⁵ or a direct bond;

10 A² is O, NR¹⁵ or a direct bond;

 A^3 is -C(=O)-, $-S(O)_2$ - or a direct bond;

each R⁶ is independently H, 1-2 CH₃, C₂-C₃ alkyl, C₁-C₃ alkoxy,

C₃-C₆ cycloalkyl, formylamino, C₂-C₄ alkylcarbonylamino,

C2-C4 alkoxycarbonylamino, NH2C(O)NH, (C1-C3 alkyl)NHC(O)NH,

(C₁-C₃ alkyl)₂NC(O)NH, N(C₁-C₃ alkyl)₂, piperidinyl, morpholinyl,

1-2 halogen, cyano or nitro;

each R⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy,

C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfinyl,

C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylthio, C₁-C₆ haloalkylsulfinyl,

C₁-C₆ haloalkylsulfonyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl,

C2-C6 haloalkynyl, C3-C6 cycloalkyl, C2-C4 alkylcarbonyl,

C2-C4 alkoxycarbonyl, halogen, cyano, nitro, hydroxy, amino,

NH(C₁-C₆ alkyl), N(C₁-C₆ alkyl)₂ or morpholinyl;

each Z is independently selected from:

25 i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl

i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl and C₂-C₁₀ alkynyl each substituted with R⁹ and optionally substituted with one or more R¹⁰;

ii) C₃-C₈ cycloalkyl, C₃-C₈ cycloalkenyl and phenyl each substituted with R⁹ and optionally substituted with one or more R¹⁰;

iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic and fused tricyclic nonaromatic heterocyclic ring systems and 5 to 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each nonaromatic or aromatic heterocyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰;

iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic

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and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing one or two nonaromatic rings that each include one or two Q as ring members and one or two ring members independently selected from C(=O) and S(O)₂, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰; and v) adamantyl substituted with R⁹ and optionally substituted with one or

- v) adamantyl substituted with R⁹ and optionally substituted with one or more R¹⁰;
- each Q is independently selected from the group -CHR¹³-, -NR¹³-, -O- and -S(O)_n-;
 - R⁸ is H, 1-2 halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy,

 C₁-C₆ haloalkoxy, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl,

 C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl,

 C₁-C₆ alkylsulfonyl, C₃-C₆ cycloalkyl, C₃-C₆ alkenyloxy,

 CO₂(C₁-C₆ alkyl), NH(C₁-C₆ alkyl), N(C₁-C₆ alkyl)₂, cyano, nitro,

 SiR¹⁹R²⁰R²¹ or GeR¹⁹R²⁰R²¹:
- R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy;

 C₁-C₆ haloalkoxy; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl;

 C₁-C₆ alkylthio; C₁-C₆ haloalkylthio; C₁-C₆ alkylsulfinyl;

 C₁-C₆ alkylsulfonyl; C₃-C₆ cycloalkyl; C₃-C₆ alkenyloxy;

 CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; -C(R¹⁸)=NOR¹⁷;

 cyano; nitro; SF₅; SiR²²R²³R²⁴; or GeR²²R²³R²⁴; or R⁹ is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl,

 pyrimidinyl, or pyrimidinyloxy each optionally substituted with one of R¹¹,

 R¹², or both R¹¹ and R¹²;
 - each R¹⁰ is independently halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, nitro or cyano; or
- when R⁹ and an R¹⁰ are attached to adjacent atoms on Z, R⁹ and said adjacently
 attached R¹⁰ can be taken together as -OCH₂O- or -OCH₂CH₂O-; each CH₂
 group of said taken together R⁹ and R¹⁰ optionally substituted with 1-2
 halogen; or
- when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is

 -CHR¹⁵O-N=C(R⁷)-, -O-N=C(R⁷)-, -O-CH₂CH₂O-N=C(R⁷)-,

 -CHR¹⁵O-C(R¹⁵)=C(R⁷)-, -CH=N-N=C(R⁷)-, -CHR¹⁵N(R¹⁵)-N=C(R⁷)- or

 -CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as -(CH₂)_r-J- such that J is attached to Z;

J is -CH₂-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -N(R¹⁶)CH₂- or -CH₂N(R¹⁶)-; each CH₂ group of said J optionally substituted with 1 to 2 CH₃; R¹¹ and R¹² are each independently 1-2 halogen; C₁-C₄ alkyl; C₁-C₄ haloalkyl; 5 C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₂-C₆ alkoxyalkyl; C₂-C₆ alkylthioalkyl; C₃-C₆ alkoxyalkynyl; C₇-C₁₀ tetrahydropyranyloxyalkynyl; benzyloxymethyl; C₁-C₄ alkoxy; C₁-C₄ haloalkoxy; C₃-C₆ alkenyloxy; C₃-C₆ haloalkenyloxy; C₃-C₆ alkynyloxy; C₃-C₆ haloalkynyloxy; C₂-C₆ alkoxyalkoxy; 10 C₅-C₉ trialkylsilylalkoxyalkoxy; C₂-C₆ alkylthioalkoxy; C₁-C₄ alkylthio; C_1 - C_4 haloalkylthio; C_1 - C_4 alkylsulfinyl; C_1 - C_4 haloalkylsulfinyl; C₁-C₄ alkylsulfonyl; C₁-C₄ haloalkylsulfonyl; C₃-C₆ alkenylthio; C₃-C₆ haloalkenylthio; C₂-C₆ alkylthioalkylthio; nitro; cyano; thiocyanato; hydroxy; $N(R^{26})_2$; SF_5 ; $Si(R^{25})_3$; $Ge(R^{25})_3$; $(R^{25})_3Si-C=C-$; $OSi(R^{25})_3$; $OGe(R^{25})_3$; $C(=O)R^{26}$; $C(=S)R^{26}$; $C(=O)OR^{26}$; $C(=S)OR^{26}$; $C(=O)SR^{26}$; 15 $C(=S)SR^{26}$; $C(=O)N(R^{26})$; $C(=S)N(R^{26})$; $OC(=O)R^{26}$; $OC(=S)R^{26}$; $SC(=O)R^{26}$; $SC(=S)R^{26}$; $N(R^{26})C(=O)R^{26}$; $N(R^{26})C(=S)R^{26}$; $OC(=O)OR^{27}$; $OC(=O)SR^{27}$; $OC(=O)N(R^{26})$; $SC(=O)OR^{27}$; $SC(=O)SR^{27}$; S(O)₂OR²⁶; S(O)₂N(R²⁶)₂; OS(O)₂R²⁷; N(R²⁶)S(O)₂R²⁷; or phenyl, phenoxy, benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or 20 pyridinylethynyl, each optionally substituted with halogen, C₁-C₄ alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano; each R¹³ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, 25 C_1 - C_4 haloalkoxy, nitro or cyano; R¹⁴ is H, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C2-C6 haloalkenyl, C2-C6 alkynyl, C2-C6 haloalkynyl or C3-C6 cycloalkyl; each R¹⁵ is independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, 30 C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; or when Y is -CHR¹⁵N(R¹⁵)C(=0)N(R¹⁵)-, the two R¹⁵ attached to nitrogen atoms on said group can be taken together as -(CH₂)₅-; or when Y is -CHR¹⁵O-N=C(R⁷)NR¹⁵-, R⁷ and the adjacently attached R¹⁵ can be taken together as -CH₂-(CH₂)_S-, -O-(CH₂)_S-, -S-(CH₂)_S- or 35 -N(C₁-C₃ alkyl)-(CH₂)_s-; with the directionality of said linkage defined such that the moiety depicted on the left side of the linkage is bonded to the carbon and the moiety on the right side of the linkage is bonded to the nitrogen;

- R¹⁶, R¹⁷ and R¹⁸ are each independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are each independently C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_1 - C_4 alkoxy or phenyl;
- each R^{25} is independently C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl, C_1 - C_4 alkoxy or phenyl;
- each R²⁶ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- each R²⁷ is independently C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

m, n and p are each independently 0, 1 or 2;

r is 0 or 1; and

20 s is 2 or 3; and

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- (2) at least one compound selected from compounds that control fungal disease by inhibiting the sterol biosynthesis pathway; wherein component (1) and component (2) are added in amounts sufficient to provide a fungicidal effectiveness greater than the sum of the fungicidal effectivenesses of the amounts of said components taken independently.
- 11. A method of Claim 10 wherein component (1) is 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and component (2) is selected from the group consisting of epoxiconazole, fenpropimorph, flusilazole, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from 15:1 to 1:15.

INTERNATIONAL SEARCH REPORT

ir attonal Application No PCT/US 98/01382

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 A01N43/653 //(A01N43/653,61:00,55:00,43:84,43:76,43:653,43:50)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) $IPC \ 6 \ A01N$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUM	ENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 00612 A (DU PONT ;BROWN RICHARD JAMES (US); CHAN DOMINIC MING TAK (US); HOW) 9 January 1997 see page 2, line 20 - page 8, line 30 see page 115, line 30 see page 115, line 33 see page 117, line 6 - line 11 see page 117, line 20 - line 32 see page 118, line 6 - page 119, line 4 see page 126; example 59	1,2,7,8, 10
Α	WO 96 03044 A (RHONE POULENC AGROCHIMIE; LATORSE MARIE PASCALE (FR)) 8 February 1996 see page 1, line 31 - page 3, line 14 -/	1-11

X Further documents are listed in the continuation of box C.	X Patent family members are listed in annex.
Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filling date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filling date but later than the priority date claimed	T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention. "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone. "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of theinternational search	Date of mailing of the International search report
2 June 1998	16/06/1998
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3016	Lamers, W

INTERNATIONAL SEARCH REPORT

In ational Application No PCT/US 98/01382

		PC1/US 98	0/01362
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		15
Category *	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
A	WO 96 27290 A (DU PONT ;BERGER RICHARD ALAN (US); REAP JAMES JOHN (US)) 12 September 1996 see page 1, line 25 - line 35 see page 2, line 16 - line 23		1-11
A	WO 97 00012 A (CIBA GEIGY AG ;KNAUF BEITER GERTRUDE (DE); KUENG RUTH BEATRICE (CH) 3 January 1997 see page 1 - page 2 		1-11
	·		
		·	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intr tional Application No
PCT/US 98/01382

Patent document cited in search report	rt	Publication date		Patent family member(s)	Publication date
WO 9700612	A	09-01-1997	AU	6177096 A	22-01-1997
			EP	0836384 A	22-04-1998
WO 9603044	A	08-02-1996	FR	2722652 A	26-01-1996
			AU	3080595 A	22-02-1996
			BG	101231 A	28-11-1997
			CA	2192989 A	08-02-1996
			CZ	9700180 A	16-04-1997
			EP	0773720 A	21-05-1997
			HU	77234 A	02-03-1998
			JP	10503192 T	24-03-1998
			PL	318328 A	09-06-1997
			SK	8697 A	10-09-1997
			ZA	9505935 A	20-02-1996
WO 9627290	A	12-09-1996	AU	5092596 A	23-09-1996
			CA	2214772 A	12-09-1996
			EP	0813363 A	29-12-1997
			PL	322102 A	05-01-1998
WO 9700012	Α	03-01-1997	AU	690464 B	23-04-1998
			AU	6125196 A	15-01-1997
			EP	0831698 A	01-04-1998